REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 25 | 2017

Interlaboratory Proficiency Test 04/2017

Metals in natural waters

Mirja Leivuori, Riitta Koivikko, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 25 | 2017

Interlaboratory Proficiency Test 04/2017

Metals in natural waters

Mirja Leivuori, Riitta Koivikko, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

Proftest
SYKE

FINAS
Finnish Accreditation Service
PT01 (EN ISO/IEC 17043)

Helsinki 2017
Finnish Environment Institute

REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 25 | 2017
Finnish Environment Institute SYKE
Proftest SYKE

Layout: Markku Ilmakunnas

The publication is also available in the Internet: www.syke.fi/publication | helda.helsinki.fi/syke

ISBN 978-952-11-4865-1 (pbk.)
ISBN 978-952-11-4866-8 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)

Author(s): Mirja Leivuori, Riitta Koivikko, Timo Sara-Aho, Teemu Näykki, Keijo Tervonen, Sari Lanteri, Ritva Väisänen and Markku Ilmakunnas

Publisher and financier of publication: Finnish Environment Institute (SYKE)
P.O. Box 140, FI-00251 Helsinki, Finland, Phone +358 295 251 000, syke.fi.

Year of issue: 2017

SYKE

ABSTRACT

Interlaboratory Proficiency Test 04/2017

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in natural and domestic waters in April-May 2017. The measurands were: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V, and Zn. Three sample types were: synthetic, domestic and natural (river) water. In total 20 participants joined in the PT. In this proficiency test 92 % of the results were satisfactory when deviation of 10–25 % from the assigned value was accepted.

Basically, either the metrologically traceable concentration, the calculated concentration, the robust mean, or the mean of the results reported by the participants was used as the assigned value for the measurands. The evaluation of the performance of the participants was carried out using z scores.
Warm thanks to all the participants of this proficiency test!

Keywords: water analysis, metals, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V, Zn, water, environmental laboratories, proficiency test, interlaboratory comparisons

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 04/2017

Proftest SYKE järjesti pätevyyskokeen ympäristönäytteitä analysoiville laboratorioille huhti-toukokuussa 2017. Pätevyyskokeessa määritettiin synteettisestä näytteestä sekä talous- ja luonnonvedestä seuraavat metallit: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V ja Zn. Pätevyyskokeeseen osallistui yhteensä 20 osallistujaa. Koko tulosaineistossa hyväksyttäviä tuloksia oli 92 %, kun vertailuarvosta sallittiin 10–25 %:n poikkeama.

Osallistujien pätevyyden arviointi tehtiin z-arvon avulla. Testisuureen vertailuarvona käytettiin metrologisesti jäljitettävää pitoisuutta, laskennallista pitoisuutta, osallistujien ilmoittamien tulosten robustia keskiarvoa tai keskiarvoa.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: vesianalyysi, metallit, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V, Zn, vesi- ja ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus

SAMMANDRAG

Provningsjämförelse 04/2017

Proftest SYKE genomförde en provningsjämförelse i april-maj 2017, som omfattade bestämningen av Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V och Zn i natur och hushållsvatten. Tillsammans 20 laboratorier deltog i jämförelsen. I jämförelsen var 92 % av alla resultaten tillfredsställande, när avvikelsen 10–25 % från referensvärdet accepterades.

Som referensvärde av analytens koncentration användes mest det metrologiska spårbara värdet, teoretiska värdet, robust medelvärdet eller medelvärdet av deltagarnas resultat.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: vattenanalyser, metaller, Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V, Zn, provningsjämförelse, vatten- och miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in natural and domestic waters in April-May 2017 (MET 04/2017). The measurands were: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V and Zn. Three sample types were: synthetic, domestic and natural (river) water. In total 20 participants joined in the PT. In the PT the results of Finnish participants providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer:

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, FI-00430 Helsinki, Finland
Phone: +358 295 251 000
e-mail: proftest@environment.fi

The responsibilities in organizing the proficiency test were as follows:

Mirja Leivuori	coordinator
Riitta Koivikko	substitute for coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance
Ritva Väisänen	technical assistance
Timo Sara-Aho	analytical expert (metals, ID-ICP-MS)
Teemu Näykki	analytical expert (Hg, ID-ICP-MS)

2.2 Participants

In total 20 participants joined in this proficiency test (Appendix 1), 16 from Finland and 4 from other EU countries. One participant reported two result sets. Altogether 95 % of the reported results were measured using accredited analytical methods at least for a part of the measurands. For this proficiency test, the organizing laboratory (T003, ISO/IEC 17025, www.finas.fi/sites/en) has the code 6 (SYKE, Helsinki).

2.3 Samples and delivery

Three types of samples were delivered to the participants: synthetic, domestic and natural (river) water. The sample preparation is described in details in the Appendix 2.

When preparing the samples, the purity of the used sample vessels was controlled. The randomly chosen sample vessels were filled with deionized water and the purity of the sample vessels was controlled after three days by analyzing Cd, Cu, Hg, and Zn. According to the test results all used vessels fulfilled the purity requirements.

The synthetic sample A1M was prepared from the NIST traceable commercial reference material produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The samples D3M and D3Hg were domestic water collected from Helsinki with additions of single element standard solutions (Merck CertiPUR®, Appendix 2). The river water was collected from Porvoo, the southern Finland, for the sample N3M and N3Hg. Some additions of single element standard solutions (Merck CertiPUR®) were used in preparation of the river water samples (Appendix 2). The water samples were acidified with nitric acid with the exception of samples for mercury, which were acidified with the hydrochloric acid.

The samples were delivered on 24 April 2017 to the international participants and on 25 April 2017 to the national participants. The samples arrived to the participants on 26 April 2017.

The samples were requested to be measured as follows:

Mercury (A1Hg, G2Hg and N3Hg)	latest on 5 May 2017
The other samples	latest on 12 May 2017

The results were requested to be reported latest on 15 May 2017. Participants delivered the results mainly accordingly, one participant reported the results on the next day. The preliminary results were delivered to the participants via ProftestWEB and email on 22 May 2017.

2.4 Homogeneity and stability studies

The homogeneity of the samples was tested by analyzing various tested measurands. More detailed information of homogeneity studies is shown in Appendix 3. According to the homogeneity test results, all samples were considered homogenous. The synthetic samples were prepared from traceable certified reference materials. However, homogeneity of these was checked by parallel measurements of two samples and they were considered homogenous.

Based on the earlier similar proficiency tests the water samples are known to be stable over the given time period for the test.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with comments to the technical execution e.g. information for the parallel results. The comments from the provider are mainly focused to recommendations for method validation. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results, which differed from the data more than $SD_{rob} \times 5$ or 50 % from the robust mean, were rejected before the statistical results handling. The replicate results were tested using the Cochran test. If the result has been reported as below detection limit, it has not been included in the statistical calculations. If the participant did not report the result of replicate measurements when requested, their result was excluded when setting the assigned value.

More information about the statistical handling of the data is available from the Guide for participant [4].

2.6.2 Assigned values

For the synthetic sample A1M the NIST traceable calculated concentrations were used as the assigned values, with the exception of B, Hg and Pb. The assigned values for Hg and Pb are based on the results of the metrologically traceable isotope dilution (ID) ICP-MS technique. Also for the samples D2M, D2Hg, N3M, and N3Hg the results based on ID-ICP-MS results were used for Hg and Pb. The ID-ICP-MS method is accredited for soluble lead in synthetic and natural waters and for soluble mercury in synthetic, natural and waste waters in the scope of the calibration laboratory (K054, ISO/IEC 17025, www.finas.fi/sites/en). Basically, for the other samples and measurands the robust mean value was used as the assigned value. If the number of results was low, the mean value was reported as the assigned value (n(stat)<12, A1M: B; D2M: As, B, Ba, Co, Ni, Sb, Se, Sr, S_{tot}, Ti, U, V; N3M: B, Sn, Sr, Ti, U).

The robust mean or the mean are not metrologically traceable assigned values. When it was not possible to have metrologically traceable assigned values, the robust mean or the mean value of the results was the best available value to be used as the assigned value. The reliability of the assigned values was statistically tested according to the IUPAC Technical report [3].

For the calculated assigned values the expanded measurement uncertainty (U_{pt}, k=2) was estimated by using the standard uncertainties associated with individual operations involved in

the sample preparation. The main individual source of the uncertainty was the uncertainty of the concentration in the stock solution.

For the metrologically traceable mercury and lead results, the uncertainty is the expanded measurement uncertainty of the ID-ICP-MS method. When the robust mean or the mean was used as the assigned value, the uncertainty was calculated using the robust standard deviation or standard deviation, respectively [2, 4].

The uncertainty of the calculated assigned value and the metrologically traceable value for metals in the synthetic samples varied between 0.5 and 6 %. When using the robust mean or the mean of the participant results as the assigned value, the uncertainties of the assigned values were between 1.6 and 10 % (Appendix 5). **After reporting the preliminary results, the uncertainty of metrologically traceable value of Hg has been changed** for the synthetic sample A1Hg and the domestic water sample D2Hg from 3 % to 6 %. The participant can re-calculate their zeta values with the formula given in the preliminary results or in the Guide for participant [4].

After reporting of the preliminary **results no changes to the assigned values have been done.**

2.6.3 Standard deviation for proficiency assessment and z score

The standard deviation for the proficiency assessment was estimated based on the uncertainty of the assigned value, the concentrations of the measurand, the results of homogeneity and stability tests, and the long-term variation in the former proficiency tests. The standard deviation for the proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 10–25 % depending on the sample and measurand. After reporting the preliminary results **no changes have been done for the standard deviations of the proficiency assessment values.**

When using the robust mean as the assigned value, the reliability was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U_{pt}) divided by 2) and s_{pt} is the standard deviation for proficiency assessment [2, 3]. When testing the reliability of the assigned value the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the target value of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation of the reported results (s_{rob}) [2, 3]. The criterion $s_{rob} / s_{pt} < 1.2$ was mainly fulfilled.

In the following cases, the criterion for the reliability of the assigned value was not met and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurand
N3M	As, Se

3 Results and conclusions

3.1 Results

The terms used in the results tables are presented in Appendix 6. The results and the performance of each participant are presented in Appendix 7 and the summary of the results in Table 1. The summaries of z scores are shown in Appendix 8. In Appendix 9 the z scores are shown in the ascending order. The reported results with their expanded uncertainties (k=2) grouped according to the methods are presented in Appendix 10.

The robust standard deviations of the results varied from 3 % to 21 % (Table 1). The robust standard deviation of results was lower than 10 % for 94 % of the results. Standard deviations higher than 10 % apply for Hg in the synthetic and domestic water samples (A1Hg, D2Hg) and for As and Se in the river water sample (N3M, Table 1). The robust standard deviations for water samples were somewhat higher than in the previous similar proficiency test MET 06/2016, where the deviations varied from 0.5 % to 15.5 % [5].

Table 1. The summary of the results in the proficiency test MET 04/2017.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2 x s_{pt} %	n (all)	Acc z %
Al	A1M	µg/l	320	317	316	322	23	7.2	10	18	78
	D2M	µg/l	44.7	44.8	44.7	45.3	2.6	5.7	15	17	94
	N3M	µg/l	2880	2900	2880	2895	124	4.3	10	19	79
As	A1M	µg/l	6.50	6.3	6.3	6.2	0.5	7.9	15	14	85
	D2M	µg/l	0.35	0.35	0.35	0.35	0.03	8.5	15	13	91
	N3M	µg/l	0.96	0.97	0.96	0.94	0.14	14.3	25	16	79
B	A1M	µg/l	35.4	35.4	35.4	35.5	1.2	3.4	10	11	91
	D2M	µg/l	10.3	10.3	10.2	10.3	0.5	5.4	10	10	78
	N3M	µg/l	17.7	17.7	17.7	17.6	1.7	9.6	20	12	82
Ba	A1M	µg/l	18.0	17.5	17.7	17.4	0.7	4.1	10	13	92
	D2M	µg/l	4.47	4.47	4.46	4.45	0.15	3.3	10	12	92
	N3M	µg/l	55.4	55.6	55.4	54.7	2.6	4.6	10	14	100
Cd	A1M	µg/l	7.1	7.02	7.01	7.07	0.37	5.2	15	17	94
	D2M	µg/l	0.42	0.41	0.42	0.42	0.03	7.3	15	15	86
	N3M	µg/l	0.62	0.62	0.62	0.62	0.04	7.1	15	18	83
Co	A1M	µg/l	5.10	4.99	4.97	4.93	0.22	4.4	10	13	100
	D2M	µg/l	0.55	0.55	0.55	0.55	0.02	3.3	15	12	100
	N3M	µg/l	1.87	1.87	1.87	1.88	0.15	7.8	15	15	100
Cr	A1M	µg/l	14.5	14.1	14.1	14.0	0.6	4.0	10	16	94
	D2M	µg/l	5.31	5.30	5.31	5.32	0.16	3.0	10	14	100
	N3M	µg/l	6.89	6.82	6.89	6.76	0.32	4.7	10	17	94
Cu	A1M	µg/l	23.3	22.8	23.0	23.0	0.9	4.0	10	18	89
	D2M	µg/l	349	349	349	350	12	3.5	10	16	100
	N3M	µg/l	22.8	22.7	22.8	22.6	1.0	4.3	10	20	95
Fe	A1M	µg/l	156	156	156	155	8	5.4	10	18	100
	D2M	µg/l	147	146	147	146	7	5.1	10	17	88
	N3M	µg/l	2749	2747	2749	2737	92	3.3	10	21	95

Table 1. The summary of the results in the proficiency test MET 04/2017.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2 x s_{pt} %	n (all)	Acc z %
Hg	A1Hg	µg/l	0.065	0.069	0.069	0.068	0.014	20.8	25	14	69
	D2Hg	µg/l	0.072	0.073	0.073	0.076	0.014	19.4	25	13	83
	N3Hg	µg/l	0.17	0.173	0.173	0.173	0.018	10.1	20	15	100
Mn	A1M	µg/l	88.0	87.6	87.6	87.5	2.6	3.0	10	17	100
	D2M	µg/l	13.1	13.1	13.1	13.1	0.6	4.8	10	17	100
	N3M	µg/l	182	183	182	182	8	4.2	10	19	100
Mo	A1M	µg/l	33.0	33.3	33.4	33.1	1.7	5.0	10	15	93
	D2M	µg/l	10.4	10.4	10.4	10.3	0.6	6.1	15	14	86
	N3M	µg/l	20.1	20.1	20.1	20.1	1.1	5.6	10	17	94
Ni	A1M	µg/l	9.50	9.5	9.4	9.4	0.5	5.2	15	16	94
	D2M	µg/l	0.49	0.49	0.50	0.50	0.04	7.2	20	14	92
	N3M	µg/l	8.40	8.41	8.40	8.38	0.40	4.8	15	18	94
Pb	A1M	µg/l	3.36	3.15	3.15	3.19	0.22	7.1	15	16	86
	D2M	µg/l	1.34	1.30	1.28	1.30	0.07	5.4	15	15	86
	N3M	µg/l	4.98	4.95	4.93	4.90	0.22	4.4	15	18	94
Sb	A1M	µg/l	15.0	14.3	14.3	14.2	1.0	6.9	10	13	77
	D2M	µg/l	4.76	4.76	4.78	4.82	0.50	10.5	20	12	92
	N3M	µg/l	9.77	9.75	9.77	9.83	0.83	8.5	20	15	87
Se	A1M	µg/l	9.90	9.90	9.65	10.00	0.76	7.8	15	12	82
	D2M	µg/l	5.34	5.34	5.33	5.32	0.48	9.0	20	10	100
	N3M	µg/l	1.43	1.46	1.43	1.42	0.20	13.7	25	13	92
Sn	A1M	µg/l	17.0	16.5	16.2	16.3	1.1	6.8	15	9	89
	D2M	µg/l	5.06	5.06	5.07	5.02	0.29	5.7	15	9	100
	N3M	µg/l	9.79	9.79	9.82	9.80	0.46	4.7	15	11	100
Sr	A1M	µg/l	22.0	21.7	21.7	21.9	1.5	6.9	10	9	100
	D2M	µg/l	40.1	40.1	40.1	40.2	2.6	6.6	15	9	100
	N3M	µg/l	71.4	71.4	71.4	71.6	4.3	6.0	15	11	100
Stot	A1M	mg/l	12.0	11.7	11.6	11.6	0.5	4.2	10	12	92
	D2M	mg/l	7.92	7.92	8.07	7.95	0.43	5.4	10	12	75
	N3M	mg/l	7.32	7.37	7.32	7.30	0.32	4.3	10	14	86
Ti	A1M	µg/l	15.0	14.8	14.8	14.8	0.7	4.6	10	9	100
	D2M	µg/l	6.57	6.57	6.65	6.55	0.32	4.8	10	8	86
	N3M	µg/l	93.8	93.8	93.7	93.7	3.3	3.5	10	10	100
U	A1M	µg/l	4.20	4.35	4.35	4.35	0.31	7.1	15	10	100
	D2M	µg/l	2.17	2.17	2.17	2.18	0.14	6.6	15	10	100
	N3M	µg/l	1.21	1.21	1.21	1.23	0.08	6.8	15	11	100
V	A1M	µg/l	5.60	5.33	5.32	5.38	0.25	4.6	10	13	85
	D2M	µg/l	5.62	5.62	5.61	5.58	0.25	4.4	10	12	92
	N3M	µg/l	5.46	5.46	5.46	5.35	0.28	5.1	10	15	100
Zn	A1M	µg/l	13.1	13.2	13.1	13.1	0.7	5.0	10	17	88
	D2M	µg/l	14.3	14.4	14.3	14.4	0.7	4.9	15	16	100
	N3M	µg/l	24.1	24.2	24.1	23.8	1.6	6.5	15	19	100

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, $2 \times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurands in the PT. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 10. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. The statistically significant differences between the results are shown in Appendix 11.

Effect of measurement methods on elemental results

The most commonly used analytical method was ICP-MS, followed by ICP-OES. Some participants used GAAS- or FAAS-techniques (Appendix 10).

In many cases the number of results was too low for the statistical comparison of the analytical methods (Appendix 10). No statistical differences between analytical techniques were observed except between ICP-MS and ICP-OES results for Al and Zn in the synthetic sample A1M and for Zn in the river water sample N3M (Appendix 11). In each case the ICP-MS results were lower than the ICP-OES results.

Recoveries that are too high may be caused by spectral interferences (overlapping wavelengths in emission spectrometry, polyatomic or isobaric interferences in mass spectrometry), matrix effects or contamination. Matrix effects can often be overcome by matrix matching the calibration standards, however this is often difficult with environmental samples since the elemental concentrations vary a lot even within the same sample type.

As a general note, a low recovery may be an indication of loss of measurand which can occur during sample pretreatment (e.g. volatilization during acid digestion) or measurement (e.g. GAAS analysis). It may also be caused by incorrect background correction (ICP-OES) or matrix effects.

According to the results of this PT, majority of the participants' results remained lower than the assigned values of Pb, Sb and V for the sample A1M. However the differences were generally within the reported measurement uncertainties of the participants.

Effect of measurement methods on mercury results

Mercury was measured mostly by using the techniques based on ICP-MS or cold vapor CV-AFS, followed by cold vapor CV-AAS technique. One participant used CV-ICP-MS for mercury (Appendix 10). Between the reported measuring methods no statistically significant differences were found. For determination of assigned value of mercury (and also lead), high accuracy isotope dilution ICP-MS method was applied.

Generally, the differences in mercury results are mainly due to different pretreatment procedures. Analytical techniques have less effect on the results, but for example using CV-AFS lower detection limits can be achieved compared to CV-AAS. CV-ICP-MS is known to have very competent detection limits as well. For water samples hydrochloric acid is recommended for sample preservation and BrCl is recommended for oxidation of mercury species.

4 Uncertainties of the results

The expanded uncertainties (k=2) of the reported results were reported by 95 % of the participants, at least for some of their results (Table 2, Appendix 10). Several approaches were used for estimating the measurement uncertainty (Appendix 12). The most used approach was based on the internal quality data with sample replicates and the method validation data [6]. MUkit measurement uncertainty software for the estimation of the uncertainties was used by at maximum six participants (Appendix 12) [7]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

The range of the reported uncertainties varied between the measurands and the sample types. As can be seen in Table 2, some of the participants have overestimated their expanded (k=2) measurement uncertainty. Very high measurement uncertainties (i.e. 50 % or higher) should not exist, unless the measured concentration is near to the limit of quantification. However, the number of under or overestimations has decreased during past few years. In this PT the participants did not report expanded uncertainties below 5%, which could commonly be considered unrealistic uncertainty value for routine laboratories.

Table 2. The range of the expanded measurement uncertainties (U_{pt}%, k=2) reported by the participants.

Measurand	A1M/A1Hg, U_{pt} %	D2M/D2Hg, U_{pt} %	N3M/N3Hg, U_{pt} %
Al	6-29	10-30	6-29
As	10-25	10-25	10-25
B	10-25	10-25	10-25
Ba	10-20	10-20	10-25
Cd	10-22	10-22	10-22
Co	10-20	10-20	10-20
Cr	10-25	10-30	10-30
Cu	9-20	10-20	9-20
Fe	8-35	10-35	8-35
Hg	7-36	7-36	7-36
Mn	7-20	8-20	7-20
Mo	10-50	10-50	10-50
Ni	10-25	10-25	10-25
Pb	10-30	10-30	10-38
Sb	8-35	8-35	8-35
Se	10-28	12-28	10-28
Sn	10-20	10-20	10-20
Sr	10-20	10-20	10-20
S_{tot}	7-20	10-20	7-20
Ti	10-30	10-30	15-30
U	10-20	10-20	10-20
V	8-21	8-21	8-21
Zn	8-29	10-29	8-29

In order to promote the enhancement of environmental measurements' quality standards and traceability, the national quality recommendations for data entered into the water quality registers have been published in Finland [8]. The recommendation for measurement uncertainties for all tested measurands in natural waters is 15 %. In this proficiency test some of the participants had their measurement uncertainties within this limit, while some did not achieve it. However, harmonization of the uncertainties estimation should be continued.

5 Evaluation of the results

The evaluation of the participants was based on the z scores, using the assigned values and the standard deviation for performance assessments (Appendix 6). The z scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

In total, 92 % of the results were satisfactory when deviation of 10–25 % from the assigned value was accepted. Altogether 95 % of the participants used accredited analytical methods at least for a part of the measurands and 94 % of their results were satisfactory. In the previous similar proficiency test MET 06/2016 the performance was satisfactory for 90 % of the results when deviation 5–25 % from the assigned value was accepted, and the sediment sample was included in the PT [5].The summary of the performance evaluation and comparison to the previous performance is presented in Table 3.

Table 3. Summary of the performance evaluation in the proficiency test MET 04/2017.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
A1M, A1Hg	90	10–25	• Difficulties in measurements for Hg (A1Hg), Al and Sb (A1M), < 80% satisfactory results. • In the previous PTs MET 06/2016 and MET 04/2015 the performance was satisfactory for 89 % and 88 % of the results, respectively [5, 8].
D2M, D2Hg	92	10–25	• Mainly good performance. • Difficulties in measurements for B and S_{tot} (D2M), < 80% satisfactory results. • In the previous PT MET 06/2016 the performance was satisfactory for 89 % of the results, when accepting deviation 15–25 % from the assigned value [5].
N3M, N3Hg	94	10–25	• Mainly good performance. • Only approximate assessment for As and Se • Difficulties in measurements for As, < 80% satisfactory results. • In the previous PTs MET 06/2016 and MET 04/2015 the performance was satisfactory for 91 % and 94 % of the results, respectively [5, 8].

The satisfactory results varied between 89 % and 91 % for the tested sample types (Table 3). For the synthetic sample A1M all results for Co, Fe, Mn, Sr and U were satisfactory. For B and Sb measurements from the sample A1M the performance was better (91 % and 77 % satisfactory results, respectively) than in the previous PT MET 08/14 (71 % and 73 % satisfactory results, respectively) [10]. The share of satisfactory results in the synthetic sample A1M was the lowest for Hg, about 69 %. The tested Hg concentration was low and the share of satisfactory results was lower than in the previous proficiency test PT MET 06/2016, where the share was 93 % for the concentration 0.501 µg/l and the allowed deviation was 20 % from the assigned value [5].

For the domestic water sample D2M all results for Co, Cr, Cu, Mn, Se, Sn, Sr, U, and Zn were satisfactory. For the natural (river) water sample N3M all results for Ba, Mn, Sn, Sr, Ti, U, V, and Zn were satisfactory. For B and Sb measurements of the sample N3M the performance was mainly at the same level (82 % and 87 % satisfactory results, respectively) than in the previous similar PT MET 08/14 (85 % and 92 % satisfactory results, respectively) [10].

6 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of elements in natural and domestic waters in April-May 2017. The measurands were: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V, and Zn. Three sample types were: synthetic, domestic and natural (river) water. In total 20 participants joined in the PT.

For the synthetic sample A1M the NIST traceable calculated concentrations were used as the assigned values with the exception of B, Hg and Pb. The assigned values for Hg and Pb were based on the results of the metrologically traceable isotope dilution (ID) ICP-MS technique. Also for the samples D2M, D2Hg, N3M, and N3Hg the results based on ID-ICP-MS results were used for Hg and Pb. Basically, for other samples and measurements the robust mean or the mean value was used as the assigned value. If the number of results was low, basically the mean value was reported as the assigned value (n(stat)<12, A1M: B; D2M: As, B, Ba, Co, Ni, Sb, Se, Sr, S_{tot}, Ti, U, V; N3M: B, Sn, Sr, Ti, U).

The uncertainty for the assigned value was estimated at the 95 % confidence interval and it was between 0.5 and 6 % for the calculated and metrologically traceable assigned values and for assigned values based on the robust mean or the mean it was between 1.6–10 %.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for proficiency assessment at 95 % confidence level. In this proficiency test 92 % of the data was regarded satisfactory when the result were accepted to deviate from the assigned values 10 to 25 %. Altogether 95 % of the participants used accredited methods at least for a part of measurements and 94 % of their results were satisfactory.

7 Summary in Finnish

Proftest SYKE järjesti ympäristönäytteitä analysoiville laboratorioille pätevyyskokeen huhti-toukokuussa 2017. Pätevyyskokeessa määritettiin Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, S_{tot}, Ti, U, V ja Zn synteettisestä näytteestä sekä talous- ja luonnonvedestä. Pätevyyskokeessa oli yhteensä 20 osallistujaa.

Testisuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa tai keskiarvoa. Lyijylle ja elohopealle käytettiin metrologisesti jäljitettävää tavoite-arvoa osalla testinäytteistä. Vertailuarvolle laskettiin mittausepävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 0,5 ja 6 % välillä laskennallista tai metrologisesti jäljitettävää pitoisuutta vertailuarvona käytettäessä ja muilla välillä 1,6 – 10 %.

Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta 10–25 %. Koko aineistossa hyväksyttäviä tuloksia oli 92 %. Osallistujista 95 % käytti akkreditoituja määritysmenetelmiä ainakin osalle määrityksistään ja näistä tuloksista oli hyväksyttäviä 94 %.

REFERENCES

1. SFS-EN ISO 17043, 2010. Conformity assessment – General requirements for Proficiency Testing.

2. ISO 13528, 2015. Statistical methods for use in proficiency testing by interlaboratory comparisons.

3. Thompson, M., Ellison, S. L. R., Wood, R., 2006. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC Technical report). Pure Appl. Chem. 78: 145-196, www.iupac.org.

4. Proftest SYKE Guide for laboratories: www.syke.fi/proftest/en → Running proficiency test www.syke.fi/download/noname/%7B3FFB2F05-9363-4208-9265-1E2CE936D48C%7D/39886.

5. Leivuori, M., Koivikko, R., Sara-Aho, T., Näykki, T., Tervonen, K., Lanteri, S., Väisänen, R. and Ilmakunnas, M. 2016. Interlaboratory Proficiency Test 06/2016. Metals in natural water and sediment. Reports of Finnish Environment Institute 31/2016. Helsinki. (http://hdl.handle.net/10138/166057).

6. Magnusson, B. Näykki. T., Hovind, H. and Krysell, M., 2012. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. NT Technical Report 537. Nordtest.

7. Näykki, T., Virtanen, A. and Leito, I., 2012. Software support for the Nordtest method of measurement uncertainty evaluation. Accred. Qual. Assur. 17: 603-612. *Mukit website: www.syke.fi/envical.*

8. Näykki, T. ja Väisänen, T. (toim.) 2016. Laatusuositukset ympäristöhallinnon vedenlaatu-kistereihin vietävälle tiedolle. Vesistä tehtävien analyyttien määritysrajat, mittausepä-varmuudet sekä säilytysajat ja -tavat. 2. uudistettu painos. Suomen ympäristökeskuksen raportteja 22/2016. 57 s. (http://hdl.handle.net/10138/163532).

9. Leivuori, M., Koivikko, R., Sara-Aho, T., Näykki, T., Tervonen, K., Lanteri, S., Väisänen, R. and Ilmakunnas, M. 2015. Interlaboratory Proficiency Test 04/2015. Metals in natural water and soil. Reports of Finnish Environment Institute 32/2015. Helsinki. (http://hdl.handle.net/10138/156303).

10. Leivuori, M., Koivikko, R., Sara-Aho, T., Näykki, T., Björklöf, K., Tervonen, K., Lanteri, S., Väisänen, R. and Ilmakunnas, M. 2015. Interlaboratory Proficiency Test 08/2014. Metals and mercury in waters. Reports of the Finnish Environment Institute 7/2015. Helsinki. (http://hdl.handle.net/10138/153641).

11. Ellison, S., L., R. and Williams, A. (Eds). (2012) Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, ISBN 978-0-948926-30-3.

12. ISO/IEC Guide 98-3:2008. Uncertainty of measurement - Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995).

APPENDIX 1: Participants in the proficiency test

Country	Institute
Finland	Ahma ympäristö Oy, Oulu
	Ahma ympäristö, Seinäjoki
	Eurofins Environment Testing Finland Oy, Lahti
	Eurofins Viljavuuspalvelu, Mikkeli
	Freeport Cobalt Oy
	Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere
	Kymen Ympäristölaboratorio Oy
	Lounais-Suomen vesi- ja ympäristötutkimus Oy, Turku
	Luonnonvarakeskus, Viikki B2-laboratorio
	Metropolilab Oy
	Nablabs Oy / Jyväskylä
	Novalab Oy
	Savo-Karjalan Ympäristötutkimus Oy, Kuopio
	SeiLab Oy
	SGS Inspection Services Oy, Kotka
	SYKE Ympäristökemia Helsinki
Norway	Eurofins Environment Norway A/S, Moss
Sweden	ACES, Stockholm University
	ALS Scandinavia AB, Luleå
	IVL, Svenska Miljöinstitutet AB, Göteborg

APPENDIX 2: Preparation of the samples

The synthetic sample A1M was prepared by diluting from the NIST traceable certified reference materials produced by Inorganic Ventures. The synthetic sample A1Hg was prepared by diluting from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc. The water samples D2M and N3M were prepared by adding some separate metal solutions (Merck CertiPUR®) into the original water sample, if the original concentration was not high enough. Samples D2Hg and N3Hg were prepared by adding from the NIST traceable AccuTrace™ Reference Standard produced by AccuStandard, Inc., if the original concentration was not high enough.

Measurand		A1M µg/l	D2M µg/l	N3M µg/l	Measurand		A1M µg/l	D2M µg/l	N3M µg/l
Al	Original	3200	41	930	Pb	Original	33	1.3	3.9
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	-	-
	Ass. value	320	44.7	2880		Ass. value	3.36	1.34	4.98
As	Original	65	0.38	0.73	Sb	Original	150	0.03	0.08
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	5.0	10
	Ass. value	6.5	0.35	0.96		Ass. value	15.0	4.76	9.77
B	Original	280	13	21	Se	Original	99	0.04	0.2
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	5.0	1.0
	Ass. value	35.4	10.3	17.7		Ass. value	9.90	5.34	1.43
Ba	Original	180	4.8	44	Sn	Original	170	0.08	0.02
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	5.0	10
	Ass. value	18.0	4.47	55.4		Ass. value	17.0	5.06	9.79
Cd	Original	71	0.003	0.06	Sr	Original	220	41	70
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	0.4	0.5		Addition	-	-	-
	Ass. value	7.1	0.42	0.62		Ass. value	22.0	40.1	71.4
Co	Original	51	0.05	1.0	Stot	Original	120000	8023	7200
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	0.5	-		Addition	-	-	-
	Ass. value	5.10	0.55	1.87		Ass. value	12000	7920	7320
Cr	Original	145	0.29	1.4	Ti	Original	150	0.87	17
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	5.0	2.0		Addition	-	5.0	-
	Ass. value	14.5	5.31	6.89		Ass. value	15.0	6.57	93.8
Cu	Original	233	27	20	U	Original	45	0.16	1.1
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	325	-		Addition	-	2.0	-
	Ass. value	23.3	349	22.8		Ass. value	7.20	2.17	1.21
Fe	Original	1550	140	890	V	Original	56	0.50	2.3
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	-	-		Addition	-	5.0	-
	Ass. value	156	147	2749		Ass. value	5.60	5.62	5.46
Mn	Original	880	3.1	110	Zn	Original	131	16	15
	Dilution	10	-	-		Dilution	10	-	-
	Addition	-	10	-		Addition	-	-	-
	Ass. value	88.0	13.1	182		Ass. value	13.1	14.3	24.1
Mo	Original	330	0.02	0.13	Measurand		A1Hg µg/l	D2Hg µg/l	N3Hg µg/l
	Dilution	10	-	-					
	Addition	-	10	20					
	Ass. value	33.0	10.4	20.1					
Ni	Original	95	0.67	6.2	Hg	Original	-	< 0.002	0.004
	Dilution	10	-	-		Dilution	-	-	-
	Addition	-	-	-		Addition	0.065	0.07	0.16
	Ass. value	9.50	0.49	8.40		Ass. value	0.065	0.072	0.17

Original = the original concentration, Addition = the addition concentration, Dilution = the ratio of dilution, Ass.value = the assigned value

APPENDIX 3: Homogeneity of the samples

The homogeneity was checked for the selected samples and measurands as duplicate measurements.

Criteria for homogeneity:

$s_{anal}/s_h<0.5$ and $s_{sam}^2<c$, where

s_h = standard deviation for testing the homogeneity
s_{anal} = analytical deviation, standard deviation of the results in a sub sample
s_{sam} = between sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$,
F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Measurand/Sample	Concentration [µg/l]	n	s_{pt} %	s_h%	s_h	s_{anal}	s_{anal}/s_h	$s_{anal}/s_h<0.5$?	s_{sam}^2	c	$s_{sam}^2<c$?
Cd/D2M	0.44	5	7.5	3	0.013	0.004	0.286	Yes	0	0.0001	Yes
Cr/D2M	5.64	5	5	2.0	0.113	0.055	0.489	Yes	0	0.009	Yes
Mo/D2M	10.9	5	7.5	1.0	0.109	0.051	0.465	Yes	0	0.008	Yes
Sb/D2M	5.41	5	10	1.1	0.060	0.028	0.465	Yes	0	0.002	Yes
Se/D2M	5.64	5	10	1.5	0.085	0.026	0.305	Yes	0.003	0.003	Yes
Sn/D2M	5.49	5	7.5	1.3	0.071	0.035	0.495	Yes	0.0001	0.004	Yes
Ti/D2M	6.46	5	5	2.8	0.181	0.09	0.493	Yes	0	0.024	Yes
U/D2M	2.28	5	7.5	0.9	0.021	0.009	0.449	Yes	0	0.0003	Yes
Zn/D2M	15.4	5	7.5	3.9	0.602	0.144	0.239	Yes	0.119	0.121	Yes
Cd/N3M	0.64	5	7.5	8.5	0.055	0.005	0.083	Yes	0.0007	0.0007	Yes
Cr/N3M	7.31	5	5	2.0	0.146	0.058	0.395	Yes	0.011	0.012	Yes
Mo/N3M	21.4	5	1.2	1.2	0.256	0.121	0.473	Yes	0	0.045	Yes
Sb/N3M	10.6	5	10	1.3	0.138	0.064	0.464	Yes	0.004	0.013	Yes
Sn/N3M	10.3	5	7.5	1.5	0.155	0.061	0.395	Yes	0	0.013	Yes
Ti/N3M	96.0	5	5	0.6	0.576	0.280	0.486	Yes	0	0.235	Yes
U/N3M	1.27	5	7.5	1.4	0.018	0.008	0.469	Yes	0	0.0002	Yes
Zn/N3M	25.1	4	7.5	6.0	1.507	0.222	0.147	Yes	0.641	0.670	Yes
Hg/D2Hg*	0.07	3	12.5	8.2	0.006	0.0003	0.045	Yes	0.00001	0.00001	Yes
Hg/N3Hg*	0.17	3	10	3.0	0.005	0.002	0.448	Yes	0	0.00003	Yes
Pb/D2M*	1.34	4	7.5	1.5	0.020	0.010	0.487	Yes	0	0.0004	Yes
Pb/N3M*	4.99	4	7.5	3.0	0.150	0.022	0.148	Yes	0.007	0.007	Yes

*) result based on the ID-ICP-MS measurement
s_{pt} % = standard deviation for proficiency assessment

Conclusion: The criteria were fulfilled for the tested measurands and the samples could be regarded as homogenous.

APPENDIX 4: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Proftest
5	Bottle of sample D2Hg had leaked. The participant did not request new sample.	The provider will pay more attention to careful closing of the bottles.
9	The sample arrival form did not open up from our electronic client interface.	The provider tested that the form worked normally. The provider recommends using the client interface via Internet Explorer.
14	The participant had not received the information letter of the PT.	Provider had sent the information letter to all customers in the customer register and it should have been reached by the customer.
14	The instruction for reporting parallel results was contradictory.	In the future the provider will be more carefully with the instructions.
21	In the preliminary results reporting, was noticed a typing error in the Appendix 4.	The provider corrected the error and the preliminary results were re-delivered to the domestic participants.

Participant	Comments to the results	Action / Proftest
10	The participant informed that they reported barium results erroneously for arsenic in the sample D2M. The corrected results were: Sample D2M As: 0.35 and 0.32 µg/l	The result was outlier in the statistical treatment, and thus did not affect the performance evaluation. If the result had been reported correctly, the result would have been satisfactory. The participant can re-calculate the z score according to the Guide for participants [4].

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
21	The participant reported below detection limit values (< 10 µg/l) for Mn in the sample D2M, though the tested concentration was high enough to be measured (assigned value 13.1 µg/l). The provider recommends the participant to validate their detection limit value.
2,7,8,10,12, 15,16,18,19, 20,21	For these participants the deviation of replicate measurements for some measurands and samples were high and their results were Cochran outliers. The provider recommends the participants to validate their deviation of replicate measurements.
All	After reporting the preliminary results, the uncertainty of metrologically traceable value of Hg has been changed for the synthetic sample A1Hg and the domestic water sample D2Hg from 3 % to 6 %. The participant can re-calculate their zeta values with the formula given in the preliminary results or in the Guide for participant [4].

APPENDIX 5: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/S_{pt}
Al	A1M	µg/l	320	2	0.6	Calculated value	0.06
	D2M	µg/l	44.7	1.6	3.6	Robust mean	0.24
	N3M	µg/l	2880	75	2.6	Robust mean	0.26
As	A1M	µg/l	6.50	0.1	0.8	Calculated value	0.05
	D2M	µg/l	0.35	0.02	4.8	Mean	0.32
	N3M	µg/l	0.96	0.10	10.0	Robust mean	0.40
B	A1M	µg/l	35.4	1.0	2.9	Mean	0.29
	D2M	µg/l	10.3	0.3	2.8	Mean	0.28
	N3M	µg/l	17.7	1.1	6.3	Mean	0.32
Ba	A1M	µg/l	18.0	0.1	0.6	Calculated value	0.06
	D2M	µg/l	4.47	0.09	2.1	Mean	0.21
	N3M	µg/l	55.4	1.7	3.1	Robust mean	0.31
Cd	A1M	µg/l	7.1	0.05	0.7	Calculated value	0.05
	D2M	µg/l	0.42	0.02	5.1	Robust mean	0.34
	N3M	µg/l	0.62	0.03	4.6	Robust mean	0.31
Co	A1M	µg/l	5.10	0.03	0.6	Calculated value	0.06
	D2M	µg/l	0.55	0.01	1.6	Mean	0.11
	N3M	µg/l	1.87	0.09	5.0	Robust mean	0.33
Cr	A1M	µg/l	14.5	0.1	0.6	Calculated value	0.06
	D2M	µg/l	5.31	0.11	2.0	Robust mean	0.20
	N3M	µg/l	6.89	0.19	2.8	Robust mean	0.28
Cu	A1M	µg/l	23.3	0.1	0.5	Calculated value	0.05
	D2M	µg/l	349	7	2.1	Robust mean	0.21
	N3M	µg/l	22.8	0.5	2.4	Robust mean	0.24
Fe	A1M	µg/l	156	1	0.6	Calculated value	0.06
	D2M	µg/l	147	5	3.1	Robust mean	0.31
	N3M	µg/l	2749	49	1.8	Robust mean	0.18
Hg	A1Hg	µg/l	0.065	0.004	6.0	ID-ICP-MS	0.24
	D2Hg	µg/l	0.072	0.004	6.0	ID-ICP-MS	0.24
	N3Hg	µg/l	0.17	0.005	3.0	ID-ICP-MS	0.15
Mn	A1M	µg/l	88.0	0.4	0.5	Calculated value	0.05
	D2M	µg/l	13.1	0.4	3.0	Robust mean	0.30
	N3M	µg/l	182	4	2.4	Robust mean	0.24
Mo	A1M	µg/l	33.0	0.2	0.7	Calculated value	0.07
	D2M	µg/l	10.4	0.4	4.1	Robust mean	0.27
	N3M	µg/l	20.1	0.7	3.4	Robust mean	0.34
Ni	A1M	µg/l	9.50	0.1	0.7	Calculated value	0.05
	D2M	µg/l	0.49	0.02	4.4	Mean	0.22
	N3M	µg/l	8.40	0.24	2.9	Robust mean	0.19
Pb	A1M	µg/l	3.36	0.10	3.0	ID-ICP-MS	0.20
	D2M	µg/l	1.34	0.04	3.0	ID-ICP-MS	0.20
	N3M	µg/l	4.98	0.15	3.0	ID-ICP-MS	0.20
Sb	A1M	µg/l	15.0	0.1	0.8	Calculated value	0.08
	D2M	µg/l	4.76	0.28	5.9	Mean	0.30
	N3M	µg/l	9.77	0.58	5.9	Robust mean	0.30

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Se	A1M	µg/l	9.90	0.06	0.6	Calculated value	0.04
	D2M	µg/l	5.34	0.27	5.0	Mean	0.25
	N3M	µg/l	1.43	0.14	9.9	Robust mean	0.40
Sn	A1M	µg/l	17.0	0.1	0.8	Calculated value	0.05
	D2M	µg/l	5.06	0.19	3.7	Mean	0.25
	N3M	µg/l	9.79	0.30	3.1	Mean	0.21
Sr	A1M	µg/l	22.0	0.2	0.7	Calculated value	0.07
	D2M	µg/l	40.1	1.6	3.9	Mean	0.26
	N3M	µg/l	71.4	2.3	3.2	Mean	0.21
Stot	A1M	mg/l	12.0	0.1	0.5	Calculated value	0.05
	D2M	mg/l	7.92	0.15	1.9	Mean	0.19
	N3M	mg/l	7.32	0.22	3.0	Robust mean	0.30
Ti	A1M	µg/l	15.0	0.1	0.7	Calculated value	0.07
	D2M	µg/l	6.57	0.16	2.5	Mean	0.25
	N3M	µg/l	93.8	1.9	2.0	Mean	0.20
U	A1M	µg/l	4.20	0.03	0.7	Calculated value	0.05
	D2M	µg/l	2.17	0.08	3.7	Mean	0.25
	N3M	µg/l	1.21	0.04	3.6	Mean	0.24
V	A1M	µg/l	5.60	0.04	0.7	Calculated value	0.07
	D2M	µg/l	5.62	0.14	2.5	Mean	0.25
	N3M	µg/l	5.46	0.18	3.3	Robust mean	0.33
Zn	A1M	µg/l	13.1	0.1	0.7	Calculated value	0.07
	D2M	µg/l	14.3	0.4	3.1	Robust mean	0.21
	N3M	µg/l	24.1	0.9	3.7	Robust mean	0.25

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= target value of the standard deviation for proficiency assessment
u_{pt}= standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 6: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participants's result	The result reported by the participant (the mean value of the replicates)
Md	Median
SD	Standard deviation
SD%	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i $(i = 1, 2 \ldots p)$:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 7: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Fe	µg/l	A1M		1.28	156	10	166	155	156	7	4.5	17
	µg/l	D2M		1.16	147	10	156	146	146	8	5.6	17
	µg/l	N3M		-0.52	2749	10	2677	2737	2747	78	2.9	21

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-3.31	320	10	267	322	317	18	5.7	15
	µg/l	D2M		-5.45	44.7	15	26.4	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-6.99	2880	10	1874	2895	2900	123	4.2	17
As	µg/l	A1M		-1.84	6.50	15	5.6	6.2	6.3	0.6	9.3	13
	µg/l	N3M		7.79	0.96	25	1.90	0.94	0.97	0.13	13.5	12
Cd	µg/l	A1M		-0.83	7.1	15	6.66	7.07	7.02	0.39	5.6	15
	µg/l	D2M		9.05	0.42	15	0.71	0.42	0.41	0.02	4.9	13
	µg/l	N3M		8.60	0.62	15	1.02	0.62	0.62	0.04	6.0	15
Cr	µg/l	A1M		-0.57	14.5	10	14.1	14.0	14.1	0.7	4.7	16
	µg/l	D2M		0.15	5.31	10	5.35	5.32	5.30	0.18	3.5	14
	µg/l	N3M		-0.74	6.89	10	6.64	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.42	23.3	10	22.8	23.0	22.8	0.9	4.1	16
	µg/l	D2M		-0.87	349	10	334	350	349	10	3.0	16
	µg/l	N3M		-0.70	22.8	10	22.0	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-1.68	156	10	143	155	156	7	4.5	17
	µg/l	D2M		-2.53	147	10	128	146	146	8	5.6	17
	µg/l	N3M		-0.56	2749	10	2673	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		-0.80	0.065	25	0.059	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		2.17	0.072	25	0.092	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		1.56	0.17	20	0.197	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-0.71	88.0	10	84.9	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-1.31	13.1	10	12.2	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-1.27	182	10	170	182	183	7	3.6	19
Ni	µg/l	A1M		-1.73	9.50	15	8.3	9.4	9.5	0.4	3.8	14
	µg/l	D2M		-3.30	0.49	20	0.33	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-7.98	8.40	15	3.37	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-2.12	3.36	15	2.83	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-2.74	1.34	15	1.07	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-1.78	4.98	15	4.32	4.90	4.95	0.15	3.0	14

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.38	320	10	326	322	317	18	5.7	15
	µg/l	D2M		0.48	44.7	15	46.3	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-0.05	2880	10	2873	2895	2900	123	4.2	17
As	µg/l	A1M		-0.33	6.50	15	6.3	6.2	6.3	0.6	9.3	13
	µg/l	D2M		0.11	0.35	15	0.35	0.35	0.35	0.03	7.5	10
	µg/l	N3M		-0.65	0.96	25	0.88	0.94	0.97	0.13	13.5	12

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
B	µg/l	A1M		0.56	35.4	10	36.4	35.5	35.4	1.6	4.5	10
	µg/l	D2M		0.49	10.3	10	10.6	10.3	10.3	0.4	3.7	7
	µg/l	N3M		0.17	17.7	20	18.0	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		-0.39	18.0	10	17.7	17.4	17.5	0.5	2.7	11
	µg/l	D2M		-0.09	4.47	10	4.45	4.45	4.47	0.15	3.4	11
	µg/l	N3M		-0.56	55.4	10	53.9	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		-0.79	7.1	15	6.68	7.07	7.02	0.39	5.6	15
	µg/l	D2M		-0.65	0.42	15	0.40	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-1.41	0.62	15	0.55	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		0.02	5.10	10	5.11	4.93	4.99	0.23	4.6	13
	µg/l	D2M		0.10	0.55	15	0.55	0.55	0.55	0.01	2.5	10
	µg/l	N3M		-0.21	1.87	15	1.84	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		0.07	14.5	10	14.6	14.0	14.1	0.7	4.7	16
	µg/l	D2M		0.19	5.31	10	5.36	5.32	5.30	0.18	3.5	14
	µg/l	N3M		0.06	6.89	10	6.91	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		0.39	23.3	10	23.8	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.03	349	10	350	350	349	10	3.0	16
	µg/l	N3M		-0.09	22.8	10	22.7	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-0.32	156	10	154	155	156	7	4.5	17
	µg/l	D2M		0.27	147	10	149	146	146	8	5.6	17
	µg/l	N3M		-0.38	2749	10	2697	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		1.07	0.065	25	0.074	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		1.08	0.072	25	0.082	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		1.50	0.17	20	0.196	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-0.16	88.0	10	87.3	87.5	87.6	3.2	3.7	16
	µg/l	D2M		0.00	13.1	10	13.1	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-0.16	182	10	181	182	183	7	3.6	19
Mo	µg/l	A1M		0.88	33.0	10	34.5	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-0.13	10.4	15	10.3	10.3	10.4	0.5	4.6	14
	µg/l	N3M		-0.05	20.1	10	20.1	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		0.15	9.50	15	9.6	9.4	9.5	0.4	3.8	14
	µg/l	D2M		-0.15	0.49	20	0.48	0.50	0.49	0.04	7.1	11
	µg/l	N3M		0.13	8.40	15	8.49	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-0.34	3.36	15	3.28	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.75	1.34	15	1.27	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.52	4.98	15	4.79	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-0.07	15.0	10	15.0	14.2	14.3	1.0	6.8	12
	µg/l	D2M		0.32	4.76	20	4.91	4.82	4.76	0.46	9.7	11
	µg/l	N3M		0.44	9.77	20	10.20	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		-0.34	9.90	15	9.65	10.00	9.90	0.40	4.1	9
	µg/l	D2M		-0.07	5.34	20	5.31	5.32	5.34	0.42	8.0	10
	µg/l	N3M		-0.31	1.43	25	1.38	1.42	1.46	0.22	15.2	12
U	µg/l	A1M		0.98	4.20	15	4.51	4.35	4.35	0.27	6.3	10
	µg/l	D2M		0.34	2.17	15	2.23	2.18	2.17	0.13	5.8	10
	µg/l	N3M		0.44	1.21	15	1.25	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-0.79	5.60	10	5.38	5.38	5.33	0.22	4.2	13
	µg/l	D2M		-0.64	5.62	10	5.44	5.58	5.62	0.24	4.2	11
	µg/l	N3M		-0.84	5.46	10	5.23	5.35	5.46	0.25	4.5	15

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Zn	µg/l	A1M		0.00	13.1	10	13.1	13.1	13.2	0.7	5.5	16
	µg/l	D2M		-0.37	14.3	15	13.9	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.64	24.1	15	23.0	23.8	24.2	1.3	5.6	19

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.38	320	10	326	322	317	18	5.7	15
	µg/l	D2M		-0.89	44.7	15	41.7	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-0.21	2880	10	2850	2895	2900	123	4.2	17
As	µg/l	A1M		-0.75	6.50	15	6.1	6.2	6.3	0.6	9.3	13
	µg/l	D2M		-1.09	0.35	15	0.32	0.35	0.35	0.03	7.5	10
	µg/l	N3M		1.13	0.96	25	1.10	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		0.22	35.4	10	35.8	35.5	35.4	1.6	4.5	10
	µg/l	D2M		-0.19	10.3	10	10.2	10.3	10.3	0.4	3.7	7
	µg/l	N3M		-0.50	17.7	20	16.8	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		-0.95	18.0	10	17.1	17.4	17.5	0.5	2.7	11
	µg/l	D2M		-0.36	4.47	10	4.39	4.45	4.47	0.15	3.4	11
	µg/l	N3M		-0.42	55.4	10	54.2	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		-0.75	7.1	15	6.70	7.07	7.02	0.39	5.6	15
	µg/l	D2M		-0.90	0.42	15	0.39	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-0.59	0.62	15	0.59	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-0.67	5.10	10	4.93	4.93	4.99	0.23	4.6	13
	µg/l	D2M		-0.34	0.55	15	0.54	0.55	0.55	0.01	2.5	10
	µg/l	N3M		0.96	1.87	15	2.01	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-0.70	14.5	10	14.0	14.0	14.1	0.7	4.7	16
	µg/l	D2M		-0.04	5.31	10	5.30	5.32	5.30	0.18	3.5	14
	µg/l	N3M		0.68	6.89	10	7.13	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.14	23.3	10	23.1	23.0	22.8	0.9	4.1	16
	µg/l	D2M		-0.32	349	10	343	350	349	10	3.0	16
	µg/l	N3M		-0.14	22.8	10	22.6	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-0.22	156	10	154	155	156	7	4.5	17
	µg/l	D2M		-0.42	147	10	144	146	146	8	5.6	17
	µg/l	N3M		-0.06	2749	10	2741	2737	2747	78	2.9	21
Hg	µg/l	A1Hg			0.065	25	*<0,1*	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg			0.072	25	*<0,1*	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		0.59	0.17	20	0.180	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-0.37	88.0	10	86.4	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-0.63	13.1	10	12.7	13.1	13.1	0.6	4.2	16
	µg/l	N3M		0.00	182	10	182	182	183	7	3.6	19
Mo	µg/l	A1M		-0.43	33.0	10	32.3	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-0.49	10.4	15	10.0	10.3	10.4	0.5	4.6	14
	µg/l	N3M		-0.31	20.1	10	19.8	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-0.34	9.50	15	9.3	9.4	9.5	0.4	3.8	14
	µg/l	D2M		-0.46	0.49	20	0.47	0.50	0.49	0.04	7.1	11
	µg/l	N3M		0.47	8.40	15	8.70	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-1.09	3.36	15	3.09	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.90	1.34	15	1.25	1.30	1.30	0.05	3.7	11
	µg/l	N3M		0.21	4.98	15	5.06	4.90	4.95	0.15	3.0	14

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Sb	µg/l	A1M		-1.05	15.0	10	14.2	14.2	14.3	1.0	6.8	12
	µg/l	D2M		-0.19	4.76	20	4.67	4.82	4.76	0.46	9.7	11
	µg/l	N3M		-0.29	9.77	20	9.49	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		0.13	9.90	15	10.00	10.00	9.90	0.40	4.1	9
	µg/l	D2M		-0.06	5.34	20	5.31	5.32	5.34	0.42	8.0	10
	µg/l	N3M		0.84	1.43	25	1.58	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		-0.71	17.0	15	16.1	16.3	16.5	1.6	9.9	9
	µg/l	D2M		-0.07	5.06	15	5.04	5.02	5.06	0.27	5.2	8
	µg/l	N3M		-0.07	9.79	15	9.74	9.80	9.79	0.47	4.8	10
Sr	µg/l	A1M		-1.53	22.0	10	20.3	21.9	21.7	1.3	6.1	9
	µg/l	D2M		-0.32	40.1	15	39.2	40.2	40.1	2.3	5.8	9
	µg/l	N3M		-0.20	71.4	15	70.3	71.6	71.4	3.8	5.3	11
Stot	mg/l	A1M		-0.67	12.0	10	11.6	11.6	11.7	0.6	4.7	12
	mg/l	D2M		-0.04	7.92	10	7.91	7.95	7.92	0.23	2.9	9
	mg/l	N3M		-0.42	7.32	10	7.17	7.30	7.37	0.38	5.1	13
Ti	µg/l	A1M			15.0	10	*<15*	14.8	14.8	0.6	4.1	8
	µg/l	D2M			6.57	10	*<15*	6.55	6.57	0.20	3.1	6
	µg/l	N3M		-0.33	93.8	10	92.3	93.7	93.8	3.0	3.2	10
U	µg/l	A1M		-0.43	4.20	15	4.07	4.35	4.35	0.27	6.3	10
	µg/l	D2M		-0.98	2.17	15	2.01	2.18	2.17	0.13	5.8	10
	µg/l	N3M		-1.43	1.21	15	1.08	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-0.61	5.60	10	5.43	5.38	5.33	0.22	4.2	13
	µg/l	D2M		-0.16	5.62	10	5.58	5.58	5.62	0.24	4.2	11
	µg/l	N3M		0.68	5.46	10	5.65	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		-1.60	13.1	10	12.1	13.1	13.2	0.7	5.5	16
	µg/l	D2M		-0.56	14.3	15	13.7	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.30	24.1	15	23.6	23.8	24.2	1.3	5.6	19

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-1.16	320	10	302	322	317	18	5.7	15
	µg/l	D2M		-0.04	44.7	15	44.6	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-1.35	2880	10	2685	2895	2900	123	4.2	17
As	µg/l	A1M		-0.84	6.50	15	6.1	6.2	6.3	0.6	9.3	13
	µg/l	D2M		-1.07	0.35	15	0.32	0.35	0.35	0.03	7.5	10
	µg/l	N3M		-1.30	0.96	25	0.80	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		-0.06	35.4	10	35.3	35.5	35.4	1.6	4.5	10
	µg/l	D2M		-2.98	10.3	10	8.8	10.3	10.3	0.4	3.7	7
	µg/l	N3M		-0.93	17.7	20	16.1	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		0.50	18.0	10	18.5	17.4	17.5	0.5	2.7	11
	µg/l	D2M		0.38	4.47	10	4.56	4.45	4.47	0.15	3.4	11
	µg/l	N3M		0.27	55.4	10	56.2	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		-0.05	7.1	15	7.08	7.07	7.02	0.39	5.6	15
	µg/l	D2M		-1.57	0.42	15	0.37	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-0.45	0.62	15	0.60	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-0.71	5.10	10	4.92	4.93	4.99	0.23	4.6	13
	µg/l	D2M		-0.15	0.55	15	0.54	0.55	0.55	0.01	2.5	10
	µg/l	N3M		0.21	1.87	15	1.90	1.88	1.87	0.13	6.9	15

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cr	µg/l	A1M		-1.03	14.5	10	13.8	14.0	14.1	0.7	4.7	16
	µg/l	D2M		-0.15	5.31	10	5.27	5.32	5.30	0.18	3.5	14
	µg/l	N3M		-0.25	6.89	10	6.81	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.43	23.3	10	22.8	23.0	22.8	0.9	4.1	16
	µg/l	D2M		-0.03	349	10	349	350	349	10	3.0	16
	µg/l	N3M		0.22	22.8	10	23.1	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		0.19	156	10	158	155	156	7	4.5	17
	µg/l	D2M		0.54	147	10	151	146	146	8	5.6	17
	µg/l	N3M		0.66	2749	10	2840	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		3.03	0.065	25	0.090	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		0.66	0.072	25	0.078	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		0.29	0.17	20	0.175	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-0.41	88.0	10	86.2	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-0.31	13.1	10	12.9	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-0.11	182	10	181	182	183	7	3.6	19
Mo	µg/l	A1M		-0.88	33.0	10	31.6	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-0.79	10.4	15	9.8	10.3	10.4	0.5	4.6	14
	µg/l	N3M		-0.05	20.1	10	20.1	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-0.18	9.50	15	9.4	9.4	9.5	0.4	3.8	14
	µg/l	D2M		0.35	0.49	20	0.51	0.50	0.49	0.04	7.1	11
	µg/l	N3M		0.17	8.40	15	8.51	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-0.20	3.36	15	3.31	3.19	3.15	0.21	6.6	13
	µg/l	D2M		0.35	1.34	15	1.38	1.30	1.30	0.05	3.7	11
	µg/l	N3M		0.09	4.98	15	5.02	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		0.13	15.0	10	15.1	14.2	14.3	1.0	6.8	12
	µg/l	D2M		-0.02	4.76	20	4.75	4.82	4.76	0.46	9.7	11
	µg/l	N3M		-0.18	9.77	20	9.59	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		-0.51	9.90	15	9.53	10.00	9.90	0.40	4.1	9
	µg/l	D2M		-0.71	5.34	20	4.96	5.32	5.34	0.42	8.0	10
	µg/l	N3M		-1.17	1.43	25	1.22	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		-1.37	17.0	15	15.3	16.3	16.5	1.6	9.9	9
	µg/l	D2M		-0.38	5.06	15	4.92	5.02	5.06	0.27	5.2	8
	µg/l	N3M		-0.65	9.79	15	9.31	9.80	9.79	0.47	4.8	10
Sr	µg/l	A1M		-1.73	22.0	10	20.1	21.9	21.7	1.3	6.1	9
	µg/l	D2M		-0.86	40.1	15	37.5	40.2	40.1	2.3	5.8	9
	µg/l	N3M		-0.85	71.4	15	66.9	71.6	71.4	3.8	5.3	11
Stot	mg/l	A1M		-2.02	12.0	10	10.8	11.6	11.7	0.6	4.7	12
	mg/l	D2M		-0.85	7.92	10	7.59	7.95	7.92	0.23	2.9	9
	mg/l	N3M		-0.94	7.32	10	6.98	7.30	7.37	0.38	5.1	13
Ti	µg/l	A1M		-0.53	15.0	10	14.6	14.8	14.8	0.6	4.1	8
	µg/l	D2M		-0.73	6.57	10	6.33	6.55	6.57	0.20	3.1	6
	µg/l	N3M		0.15	93.8	10	94.5	93.7	93.8	3.0	3.2	10
U	µg/l	A1M		0.70	4.20	15	4.42	4.35	4.35	0.27	6.3	10
	µg/l	D2M		0.12	2.17	15	2.19	2.18	2.17	0.13	5.8	10
	µg/l	N3M		0.22	1.21	15	1.23	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-1.09	5.60	10	5.30	5.38	5.33	0.22	4.2	13
	µg/l	D2M		-0.46	5.62	10	5.49	5.58	5.62	0.24	4.2	11
	µg/l	N3M		-0.82	5.46	10	5.24	5.35	5.46	0.25	4.5	15

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Zn	µg/l	A1M		-0.08	13.1	10	13.1	13.1	13.2	0.7	5.5	16
	µg/l	D2M		-0.28	14.3	15	14.0	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.14	24.1	15	23.9	23.8	24.2	1.3	5.6	19

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-1.19	320	10	301	322	317	18	5.7	15
	µg/l	D2M		0.00	44.7	15	44.7	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-0.26	2880	10	2843	2895	2900	123	4.2	17
As	µg/l	A1M		0.49	6.50	15	6.7	6.2	6.3	0.6	9.3	13
	µg/l	D2M		1.24	0.35	15	0.38	0.35	0.35	0.03	7.5	10
	µg/l	N3M		0.75	0.96	25	1.05	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		0.17	35.4	10	35.7	35.5	35.4	1.6	4.5	10
	µg/l	D2M		0.97	10.3	10	10.8	10.3	10.3	0.4	3.7	7
	µg/l	N3M		0.93	17.7	20	19.4	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		0.28	18.0	10	18.3	17.4	17.5	0.5	2.7	11
	µg/l	D2M		1.48	4.47	10	4.80	4.45	4.47	0.15	3.4	11
	µg/l	N3M		0.79	55.4	10	57.6	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		0.15	7.1	15	7.18	7.07	7.02	0.39	5.6	15
	µg/l	D2M		0.35	0.42	15	0.43	0.42	0.41	0.02	4.9	13
	µg/l	N3M		0.22	0.62	15	0.63	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-0.31	5.10	10	5.02	4.93	4.99	0.23	4.6	13
	µg/l	D2M		0.53	0.55	15	0.57	0.55	0.55	0.01	2.5	10
	µg/l	N3M		0.43	1.87	15	1.93	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-0.14	14.5	10	14.4	14.0	14.1	0.7	4.7	16
	µg/l	D2M		1.07	5.31	10	5.60	5.32	5.30	0.18	3.5	14
	µg/l	N3M		1.07	6.89	10	7.26	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.21	23.3	10	23.1	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.49	349	10	358	350	349	10	3.0	16
	µg/l	N3M		0.39	22.8	10	23.3	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-1.15	156	10	147	155	156	7	4.5	17
	µg/l	D2M		-0.34	147	10	145	146	146	8	5.6	17
	µg/l	N3M		-0.53	2749	10	2676	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		-0.01	0.065	25	0.065	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		-0.15	0.072	25	0.071	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		-0.06	0.17	20	0.169	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-0.07	88.0	10	87.7	87.5	87.6	3.2	3.7	16
	µg/l	D2M		0.99	13.1	10	13.8	13.1	13.1	0.6	4.2	16
	µg/l	N3M		0.88	182	10	190	182	183	7	3.6	19
Mo	µg/l	A1M		0.52	33.0	10	33.9	33.1	33.3	1.8	5.3	14
	µg/l	D2M		0.38	10.4	15	10.7	10.3	10.4	0.5	4.6	14
	µg/l	N3M		1.04	20.1	10	21.2	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-0.16	9.50	15	9.4	9.4	9.5	0.4	3.8	14
	µg/l	D2M		0.60	0.49	20	0.52	0.50	0.49	0.04	7.1	11
	µg/l	N3M		0.35	8.40	15	8.62	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-0.20	3.36	15	3.31	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.35	1.34	15	1.31	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.17	4.98	15	4.92	4.90	4.95	0.15	3.0	14

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Sb	µg/l	A1M		0.07	15.0	10	15.1	14.2	14.3	1.0	6.8	12
	µg/l	D2M		1.38	4.76	20	5.42	4.82	4.76	0.46	9.7	11
	µg/l	N3M		0.85	9.77	20	10.60	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		0.67	9.90	15	10.40	10.00	9.90	0.40	4.1	9
	µg/l	D2M		0.91	5.34	20	5.83	5.32	5.34	0.42	8.0	10
	µg/l	N3M		0.48	1.43	25	1.52	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		0.00	17.0	15	17.0	16.3	16.5	1.6	9.9	9
	µg/l	D2M		0.95	5.06	15	5.42	5.02	5.06	0.27	5.2	8
	µg/l	N3M		0.42	9.79	15	10.10	9.80	9.79	0.47	4.8	10
Sr	µg/l	A1M		-0.09	22.0	10	21.9	21.9	21.7	1.3	6.1	9
	µg/l	D2M		0.40	40.1	15	41.3	40.2	40.1	2.3	5.8	9
	µg/l	N3M		0.46	71.4	15	73.9	71.6	71.4	3.8	5.3	11
Stot	mg/l	A1M		-0.75	12.0	10	11.6	11.6	11.7	0.6	4.7	12
	mg/l	D2M		0.08	7.92	10	7.95	7.95	7.92	0.23	2.9	9
	mg/l	N3M		-0.04	7.32	10	7.31	7.30	7.37	0.38	5.1	13
Ti	µg/l	A1M		-0.27	15.0	10	14.8	14.8	14.8	0.6	4.1	8
	µg/l	D2M		0.44	6.57	10	6.72	6.55	6.57	0.20	3.1	6
	µg/l	N3M		1.17	93.8	10	99.3	93.7	93.8	3.0	3.2	10
U	µg/l	A1M		1.24	4.20	15	4.59	4.35	4.35	0.27	6.3	10
	µg/l	D2M		0.58	2.17	15	2.27	2.18	2.17	0.13	5.8	10
	µg/l	N3M		0.44	1.21	15	1.25	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-0.43	5.60	10	5.48	5.38	5.33	0.22	4.2	13
	µg/l	D2M		1.10	5.62	10	5.93	5.58	5.62	0.24	4.2	11
	µg/l	N3M		0.93	5.46	10	5.72	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		0.08	13.1	10	13.2	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.70	14.3	15	15.1	14.4	14.4	0.7	5.1	16
	µg/l	N3M		0.61	24.1	15	25.2	23.8	24.2	1.3	5.6	19

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.22	320	10	317	322	317	18	5.7	15
	µg/l	D2M		0.18	44.7	15	45.3	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-0.40	2880	10	2822	2895	2900	123	4.2	17
As	µg/l	A1M			6.50	15	*<10*	6.2	6.3	0.6	9.3	13
	µg/l	D2M			0.35	15	*<10*	0.35	0.35	0.03	7.5	10
	µg/l	N3M			0.96	25	*<10*	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		-0.08	35.4	10	35.3	35.5	35.4	1.6	4.5	10
	µg/l	D2M			10.3	10	*<40*	10.3	10.3	0.4	3.7	7
	µg/l	N3M			17.7	20	*<40*	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		3.94	18.0	10	21.6	17.4	17.5	0.5	2.7	11
	µg/l	D2M		17.81	4.47	10	8.45	4.45	4.47	0.15	3.4	11
	µg/l	N3M		0.69	55.4	10	57.3	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		0.75	7.1	15	7.50	7.07	7.02	0.39	5.6	15
	µg/l	D2M			0.42	15	*<1*	0.42	0.41	0.02	4.9	13
	µg/l	N3M		8.17	0.62	15	1.00	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-0.59	5.10	10	4.95	4.93	4.99	0.23	4.6	13
	µg/l	D2M			0.55	15	*<1.5*	0.55	0.55	0.01	2.5	10
	µg/l	N3M		-1.57	1.87	15	1.65	1.88	1.87	0.13	6.9	15

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cr	µg/l	A1M		-0.97	14.5	10	13.8	14.0	14.1	0.7	4.7	16
	µg/l	D2M		-1.73	5.31	10	4.85	5.32	5.30	0.18	3.5	14
	µg/l	N3M		-1.86	6.89	10	6.25	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.17	23.3	10	23.1	23.0	22.8	0.9	4.1	16
	µg/l	D2M		-0.35	349	10	343	350	349	10	3.0	16
	µg/l	N3M		-0.26	22.8	10	22.5	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-1.02	156	10	148	155	156	7	4.5	17
	µg/l	D2M		-1.01	147	10	140	146	146	8	5.6	17
	µg/l	N3M		-0.51	2749	10	2680	2737	2747	78	2.9	21
Mn	µg/l	A1M		-0.05	88.0	10	87.8	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-0.69	13.1	10	12.7	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-0.62	182	10	176	182	183	7	3.6	19
Mo	µg/l	A1M		-0.55	33.0	10	32.1	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-2.31	10.4	15	8.6	10.3	10.4	0.5	4.6	14
	µg/l	N3M		-1.94	20.1	10	18.2	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		0.42	9.50	15	9.8	9.4	9.5	0.4	3.8	14
	µg/l	D2M			0.49	20	*<3*	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-0.56	8.40	15	8.05	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M			3.36	15	*<10*	3.19	3.15	0.21	6.6	13
	µg/l	D2M			1.34	15	*<10*	1.30	1.30	0.05	3.7	11
	µg/l	N3M			4.98	15	*<10*	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-3.27	15.0	10	12.6	14.2	14.3	1.0	6.8	12
	µg/l	D2M		-1.81	4.76	20	3.90	4.82	4.76	0.46	9.7	11
	µg/l	N3M		-2.12	9.77	20	7.70	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		-3.23	9.90	15	7.50	10.00	9.90	0.40	4.1	9
Stot	mg/l	A1M		-0.01	12.0	10	12.0	11.6	11.7	0.6	4.7	12
	mg/l	D2M		0.70	7.92	10	8.20	7.95	7.92	0.23	2.9	9
	mg/l	N3M		0.37	7.32	10	7.46	7.30	7.37	0.38	5.1	13
V	µg/l	A1M		-2.32	5.60	10	4.95	5.38	5.33	0.22	4.2	13
	µg/l	D2M		0.11	5.62	10	5.65	5.58	5.62	0.24	4.2	11
	µg/l	N3M		1.43	5.46	10	5.85	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		2.52	13.1	10	14.8	13.1	13.2	0.7	5.5	16
	µg/l	D2M		1.96	14.3	15	16.4	14.4	14.4	0.7	5.1	16
	µg/l	N3M		1.27	24.1	15	26.4	23.8	24.2	1.3	5.6	19

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		1.29	320	10	341	322	317	18	5.7	15
	µg/l	D2M		0.52	44.7	15	46.4	45.3	44.8	2.5	5.7	16
	µg/l	N3M		0.54	2880	10	2958	2895	2900	123	4.2	17
As	µg/l	A1M		-2.60	6.50	15	5.2	6.2	6.3	0.6	9.3	13
	µg/l	D2M		0.74	0.35	15	0.37	0.35	0.35	0.03	7.5	10
	µg/l	N3M		1.43	0.96	25	1.13	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		1.57	35.4	10	38.2	35.5	35.4	1.6	4.5	10
	µg/l	D2M		-1.41	10.3	10	9.6	10.3	10.3	0.4	3.7	7
	µg/l	N3M		0.44	17.7	20	18.5	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		1.60	18.0	10	19.4	17.4	17.5	0.5	2.7	11
	µg/l	D2M		0.95	4.47	10	4.68	4.45	4.47	0.15	3.4	11
	µg/l	N3M		1.83	55.4	10	60.5	54.7	55.6	2.5	4.6	14

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cd	µg/l	A1M		-1.57	7.1	15	6.27	7.07	7.02	0.39	5.6	15
	µg/l	D2M		-0.35	0.42	15	0.41	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-0.26	0.62	15	0.61	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		1.30	5.10	10	5.43	4.93	4.99	0.23	4.6	13
	µg/l	D2M		0.28	0.55	15	0.56	0.55	0.55	0.01	2.5	10
	µg/l	N3M		-0.80	1.87	15	1.76	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-2.65	14.5	10	12.6	14.0	14.1	0.7	4.7	16
	µg/l	D2M		0.63	5.31	10	5.48	5.32	5.30	0.18	3.5	14
	µg/l	N3M		-0.52	6.89	10	6.71	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-2.47	23.3	10	20.4	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.72	349	10	362	350	349	10	3.0	16
	µg/l	N3M		-0.38	22.8	10	22.4	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		1.51	156	10	168	155	156	7	4.5	17
	µg/l	D2M		1.03	147	10	155	146	146	8	5.6	17
	µg/l	N3M		1.12	2749	10	2903	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		5.11	0.065	25	0.107	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		-1.83	0.072	25	0.056	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		-1.82	0.17	20	0.139	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		1.45	88.0	10	94.4	87.5	87.6	3.2	3.7	16
	µg/l	D2M		1.26	13.1	10	13.9	13.1	13.1	0.6	4.2	16
	µg/l	N3M		1.31	182	10	194	182	183	7	3.6	19
Mo	µg/l	A1M		-1.79	33.0	10	30.0	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-0.09	10.4	15	10.3	10.3	10.4	0.5	4.6	14
	µg/l	N3M		-1.08	20.1	10	19.0	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-2.16	9.50	15	8.0	9.4	9.5	0.4	3.8	14
	µg/l	D2M		0.67	0.49	20	0.52	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-0.63	8.40	15	8.00	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-1.40	3.36	15	3.01	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.39	1.34	15	1.30	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.30	4.98	15	4.87	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-3.30	15.0	10	12.5	14.2	14.3	1.0	6.8	12
	µg/l	D2M		-0.95	4.76	20	4.31	4.82	4.76	0.46	9.7	11
	µg/l	N3M		-1.62	9.77	20	8.19	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		-2.75	9.90	15	7.86	10.00	9.90	0.40	4.1	9
	µg/l	D2M		-1.31	5.34	20	4.64	5.32	5.34	0.42	8.0	10
	µg/l	N3M		3.11	1.43	25	1.99	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		-1.23	17.0	15	15.4	16.3	16.5	1.6	9.9	9
	µg/l	D2M		-1.24	5.06	15	4.59	5.02	5.06	0.27	5.2	8
	µg/l	N3M		-1.33	9.79	15	8.81	9.80	9.79	0.47	4.8	10
Sr	µg/l	A1M		1.60	22.0	10	23.8	21.9	21.7	1.3	6.1	9
	µg/l	D2M		0.86	40.1	15	42.7	40.2	40.1	2.3	5.8	9
	µg/l	N3M		0.99	71.4	15	76.7	71.6	71.4	3.8	5.3	11
Stot	mg/l	A1M		-1.22	12.0	10	11.3	11.6	11.7	0.6	4.7	12
	mg/l	D2M		-0.59	7.92	10	7.69	7.95	7.92	0.23	2.9	9
	mg/l	N3M		-0.80	7.32	10	7.03	7.30	7.37	0.38	5.1	13
Ti	µg/l	A1M		0.95	15.0	10	15.7	14.8	14.8	0.6	4.1	8
	µg/l	D2M		7.56	6.57	10	9.05	6.55	6.57	0.20	3.1	6
	µg/l	N3M		0.87	93.8	10	97.9	93.7	93.8	3.0	3.2	10

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
U	µg/l	A1M		-0.61	4.20	15	4.01	4.35	4.35	0.27	6.3	10
	µg/l	D2M		-0.05	2.17	15	2.16	2.18	2.17	0.13	5.8	10
	µg/l	N3M		-0.56	1.21	15	1.16	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-2.24	5.60	10	4.97	5.38	5.33	0.22	4.2	13
	µg/l	D2M		0.02	5.62	10	5.63	5.58	5.62	0.24	4.2	11
	µg/l	N3M		-0.54	5.46	10	5.31	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		0.08	13.1	10	13.1	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.10	14.3	15	14.4	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.24	24.1	15	23.7	23.8	24.2	1.3	5.6	19

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		1.11	320	10	338	322	317	18	5.7	15
	µg/l	N3M		0.55	2880	10	2959	2895	2900	123	4.2	17
B	µg/l	A1M		-1.95	35.4	10	32.0	35.5	35.4	1.6	4.5	10
	µg/l	N3M		-1.61	17.7	20	14.9	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		-0.44	18.0	10	17.6	17.4	17.5	0.5	2.7	11
	µg/l	N3M		-0.83	55.4	10	53.1	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		-0.28	7.1	15	6.95	7.07	7.02	0.39	5.6	15
	µg/l	N3M		1.72	0.62	15		0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-0.98	5.10	10	4.85	4.93	4.99	0.23	4.6	13
	µg/l	N3M		1.28	1.87	15	2.05	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-0.41	14.5	10	14.2	14.0	14.1	0.7	4.7	16
	µg/l	N3M		-0.41	6.89	10	6.75	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.64	23.3	10	22.6	23.0	22.8	0.9	4.1	16
	µg/l	N3M		-0.18	22.8	10	22.6	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-0.81	156	10	150	155	156	7	4.5	17
	µg/l	N3M		-0.56	2749	10	2672	2737	2747	78	2.9	21
Mn	µg/l	A1M		-0.53	88.0	10	85.7	87.5	87.6	3.2	3.7	16
	µg/l	N3M		-0.87	182	10	174	182	183	7	3.6	19
Mo	µg/l	A1M		-0.39	33.0	10	32.4	33.1	33.3	1.8	5.3	14
	µg/l	N3M		-1.24	20.1	10	18.9	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		0.21	9.50	15	9.7	9.4	9.5	0.4	3.8	14
	µg/l	N3M		0.71	8.40	15	8.85	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M			3.36	15	*<5*	3.19	3.15	0.21	6.6	13
	µg/l	N3M		2.60	4.98	15	5.95	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		0.07	15.0	10	15.1	14.2	14.3	1.0	6.8	12
	µg/l	N3M		0.13	9.77	20	9.90	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M			9.90	15	*<15*	10.00	9.90	0.40	4.1	9
	µg/l	N3M			1.43	25	*<15*	1.42	1.46	0.22	15.2	12
Stot	mg/l	A1M		-1.08	12.0	10	11.4	11.6	11.7	0.6	4.7	12
	mg/l	N3M		-0.51	7.32	10	7.13	7.30	7.37	0.38	5.1	13
Ti	µg/l	A1M		-0.80	15.0	10	14.4	14.8	14.8	0.6	4.1	8
	µg/l	N3M		-0.87	93.8	10	89.7	93.7	93.8	3.0	3.2	10
V	µg/l	A1M		-1.43	5.60	10	5.20	5.38	5.33	0.22	4.2	13
	µg/l	N3M		-0.40	5.46	10	5.35	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		-0.15	13.1	10	13.0	13.1	13.2	0.7	5.5	16
	µg/l	N3M		0.83	24.1	15	25.6	23.8	24.2	1.3	5.6	19

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		3.65	320	10	378	322	317	18	5.7	15
	µg/l	D2M		0.91	44.7	15	47.7	45.3	44.8	2.5	5.7	16
	µg/l	N3M		0.19	2880	10	2908	2895	2900	123	4.2	17
As	µg/l	A1M		-0.26	6.50	15	6.4	6.2	6.3	0.6	9.3	13
	µg/l	D2M		152.38	0.35	15	4.35	0.35	0.35	0.03	7.5	10
	µg/l	N3M		-0.46	0.96	25	0.91	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		6.55	35.4	10	47.0	35.5	35.4	1.6	4.5	10
	µg/l	D2M		19.32	10.3	10	20.3	10.3	10.3	0.4	3.7	7
	µg/l	N3M		6.95	17.7	20	30.0	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		-1.11	18.0	10	17.0	17.4	17.5	0.5	2.7	11
	µg/l	D2M		-0.54	4.47	10	4.35	4.45	4.47	0.15	3.4	11
	µg/l	N3M		-0.66	55.4	10	53.6	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		0.51	7.1	15	7.37	7.07	7.02	0.39	5.6	15
	µg/l	D2M		4.44	0.42	15	0.56	0.42	0.41	0.02	4.9	13
	µg/l	N3M		4.09	0.62	15	0.81	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-1.75	5.10	10	4.66	4.93	4.99	0.23	4.6	13
	µg/l	D2M		-0.48	0.55	15	0.53	0.55	0.55	0.01	2.5	10
	µg/l	N3M		-1.57	1.87	15	1.65	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-0.86	14.5	10	13.9	14.0	14.1	0.7	4.7	16
	µg/l	D2M		-0.23	5.31	10	5.25	5.32	5.30	0.18	3.5	14
	µg/l	N3M		-0.89	6.89	10	6.59	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		0.04	23.3	10	23.4	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.82	349	10	363	350	349	10	3.0	16
	µg/l	N3M		-0.19	22.8	10	22.6	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		0.20	156	10	158	155	156	7	4.5	17
	µg/l	D2M		-0.59	147	10	143	146	146	8	5.6	17
	µg/l	N3M		-0.59	2749	10	2669	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		1.24	0.065	25	0.075	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		1.03	0.072	25	0.081	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		0.17	0.17	20	0.173	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-0.60	88.0	10	85.4	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-0.59	13.1	10	12.7	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-0.67	182	10	176	182	183	7	3.6	19
Mo	µg/l	A1M		0.10	33.0	10	33.2	33.1	33.3	1.8	5.3	14
	µg/l	D2M		11.04	10.4	15	19.0	10.3	10.4	0.5	4.6	14
	µg/l	N3M		0.27	20.1	10	20.4	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-0.14	9.50	15	9.4	9.4	9.5	0.4	3.8	14
	µg/l	D2M		1.12	0.49	20	0.55	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-0.28	8.40	15	8.23	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-0.52	3.36	15	3.23	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.20	1.34	15	1.32	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.50	4.98	15	4.80	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-1.07	15.0	10	14.2	14.2	14.3	1.0	6.8	12
	µg/l	D2M		0.28	4.76	20	4.90	4.82	4.76	0.46	9.7	11
	µg/l	N3M		0.06	9.77	20	9.83	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		0.24	9.90	15	10.08	10.00	9.90	0.40	4.1	9
	µg/l	D2M		1.36	5.34	20	6.07	5.32	5.34	0.42	8.0	10
	µg/l	N3M		-1.09	1.43	25	1.24	1.42	1.46	0.22	15.2	12

Participant 9													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result		Md	Mean	SD	SD%	n (stat)
Sn	µg/l	A1M		-1.80	17.0	15	14.7	16.3	16.5	1.6	9.9	9	
	µg/l	D2M			5.06	15	*<20*	5.02	5.06	0.27	5.2	8	
	µg/l	N3M			9.79	15	*<20*	9.80	9.79	0.47	4.8	10	
Sr	µg/l	A1M		0.41	22.0	10	22.5	21.9	21.7	1.3	6.1	9	
	µg/l	D2M		0.03	40.1	15	40.2	40.2	40.1	2.3	5.8	9	
	µg/l	N3M		0.22	71.4	15	72.6	71.6	71.4	3.8	5.3	11	
Stot	mg/l	A1M		1.56	12.0	10	12.9	11.6	11.7	0.6	4.7	12	
	mg/l	D2M		2.23	7.92	10	8.80	7.95	7.92	0.23	2.9	9	
	mg/l	N3M		2.43	7.32	10	8.21	7.30	7.37	0.38	5.1	13	
Ti	µg/l	A1M		-1.60	15.0	10	13.8	14.8	14.8	0.6	4.1	8	
	µg/l	D2M		0.85	6.57	10	6.85	6.55	6.57	0.20	3.1	6	
	µg/l	N3M		0.14	93.8	10	94.5	93.7	93.8	3.0	3.2	10	
U	µg/l	A1M		-0.54	4.20	15	4.03	4.35	4.35	0.27	6.3	10	
	µg/l	D2M		-1.11	2.17	15	1.99	2.18	2.17	0.13	5.8	10	
	µg/l	N3M		-1.16	1.21	15	1.11	1.23	1.21	0.07	6.0	11	
V	µg/l	A1M		-1.43	5.60	10	5.20	5.38	5.33	0.22	4.2	13	
	µg/l	D2M		-0.43	5.62	10	5.50	5.58	5.62	0.24	4.2	11	
	µg/l	N3M		-1.28	5.46	10	5.11	5.35	5.46	0.25	4.5	15	
Zn	µg/l	A1M		0.31	13.1	10	13.3	13.1	13.2	0.7	5.5	16	
	µg/l	D2M		-0.54	14.3	15	13.7	14.4	14.4	0.7	5.1	16	
	µg/l	N3M		-0.59	24.1	15	23.0	23.8	24.2	1.3	5.6	19	

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	N3M		1.18	2880	10	3050	2895	2900	123	4.2	17
As	µg/l	N3M		-0.87	0.96	25	0.86	0.94	0.97	0.13	13.5	12
B	µg/l	N3M		2.01	17.7	20	21.3	17.6	17.7	1.8	9.9	10
Ba	µg/l	N3M		1.71	55.4	10	60.2	54.7	55.6	2.5	4.6	14
Cd	µg/l	N3M		0.27	0.62	15	0.63	0.62	0.62	0.04	6.0	15
Co	µg/l	N3M		0.29	1.87	15	1.91	1.88	1.87	0.13	6.9	15
Cr	µg/l	N3M		3.41	6.89	10	8.07	6.76	6.82	0.26	3.8	17
Cu	µg/l	N3M		1.84	22.8	10	24.9	22.6	22.7	0.7	3.2	20
Fe	µg/l	N3M		2.55	2749	10	3100	2737	2747	78	2.9	21
Hg	µg/l	N3Hg		-0.94	0.17	20	0.154	0.173	0.173	0.016	9.6	15
Mn	µg/l	N3M		1.04	182	10	192	182	183	7	3.6	19
Mo	µg/l	N3M		1.34	20.1	10	21.5	20.1	20.1	1.1	5.5	17
Ni	µg/l	N3M		0.73	8.40	15	8.86	8.38	8.41	0.37	4.4	17
Pb	µg/l	N3M		0.58	4.98	15	5.20	4.90	4.95	0.15	3.0	14
Sb	µg/l	N3M		0.75	9.77	20	10.50	9.83	9.75	0.80	8.2	13
Se	µg/l	N3M		-0.59	1.43	25	1.33	1.42	1.46	0.22	15.2	12
Sn	µg/l	N3M		0.83	9.79	15	10.40	9.80	9.79	0.47	4.8	10
Sr	µg/l	N3M		0.67	71.4	15	75.0	71.6	71.4	3.8	5.3	11
Stot	mg/l	N3M		-0.07	7.32	10	7.30	7.30	7.37	0.38	5.1	13
U	µg/l	N3M		0.88	1.21	15	1.29	1.23	1.21	0.07	6.0	11
V	µg/l	N3M		0.48	5.46	10	5.59	5.35	5.46	0.25	4.5	15
Zn	µg/l	N3M		1.33	24.1	15	26.5	23.8	24.2	1.3	5.6	19

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-0.99	320	10	304.1	322	317	18	5.7	15
	µg/l	D2M		-1.01	44.7	15	41.31	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-2.42	2880	10	2531	2895	2900	123	4.2	17
Cd	µg/l	A1M		-0.35	7.1	15	6.911	7.07	7.02	0.39	5.6	15
	µg/l	D2M		-0.81	0.42	15	0.3945	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-0.91	0.62	15	0.5775	0.62	0.62	0.04	6.0	15
Cu	µg/l	A1M		-0.58	23.3	10	22.63	23.0	22.8	0.9	4.1	16
	µg/l	D2M		-0.76	349	10	335.8	350	349	10	3.0	16
	µg/l	N3M		-1.01	22.8	10	21.65	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		1.68	156	10	169.1	155	156	7	4.5	17
	µg/l	D2M		-0.14	147	10	146.0	146	146	8	5.6	17
	µg/l	N3M		-0.59	2749	10	2668	2737	2747	78	2.9	21
Mn	µg/l	A1M		-0.16	88.0	10	87.30	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-0.92	13.1	10	12.50	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-0.98	182	10	173.1	182	183	7	3.6	19
Mo	µg/l	A1M		1.37	33.0	10	35.26	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-0.26	10.4	15	10.20	10.3	10.4	0.5	4.6	14
	µg/l	N3M		0.54	20.1	10	20.64	20.1	20.1	1.1	5.5	17
Pb	µg/l	A1M		-1.12	3.36	15	3.079	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.55	1.34	15	1.285	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.84	4.98	15	4.677	4.90	4.95	0.15	3.0	14
Zn	µg/l	A1M		-1.10	13.1	10	12.38	13.1	13.2	0.7	5.5	16
	µg/l	D2M		-1.31	14.3	15	12.89	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-1.81	24.1	15	20.82	23.8	24.2	1.3	5.6	19

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.13	320	10	322	322	317	18	5.7	15
	µg/l	D2M		0.57	44.7	15	46.6	45.3	44.8	2.5	5.7	16
	µg/l	N3M		0.38	2880	10	2934	2895	2900	123	4.2	17
As	µg/l	A1M		-0.78	6.50	15	6.1	6.2	6.3	0.6	9.3	13
	µg/l	D2M		-0.97	0.35	15	0.32	0.35	0.35	0.03	7.5	10
	µg/l	N3M		-0.03	0.96	25	0.96	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		0.20	35.4	10	35.8	35.5	35.4	1.6	4.5	10
	µg/l	D2M		0.10	10.3	10	10.4	10.3	10.3	0.4	3.7	7
	µg/l	N3M		0.08	17.7	20	17.9	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		-0.67	18.0	10	17.4	17.4	17.5	0.5	2.7	11
	µg/l	D2M		-0.67	4.47	10	4.32	4.45	4.47	0.15	3.4	11
	µg/l	N3M		-0.94	55.4	10	52.8	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		-0.86	7.1	15	6.64	7.07	7.02	0.39	5.6	15
	µg/l	D2M		0.00	0.42	15	0.42	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-0.04	0.62	15	0.62	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-1.22	5.10	10	4.79	4.93	4.99	0.23	4.6	13
	µg/l	D2M		0.05	0.55	15	0.55	0.55	0.55	0.01	2.5	10
	µg/l	N3M		-0.36	1.87	15	1.82	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-1.10	14.5	10	13.7	14.0	14.1	0.7	4.7	16
	µg/l	D2M		-0.90	5.31	10	5.07	5.32	5.30	0.18	3.5	14
	µg/l	N3M		-0.49	6.89	10	6.72	6.76	6.82	0.26	3.8	17

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Cu	µg/l	A1M		-1.37	23.3	10	21.7	23.0	22.8	0.9	4.1	16
	µg/l	D2M		-0.92	349	10	333	350	349	10	3.0	16
	µg/l	N3M		-1.23	22.8	10	21.4	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		1.41	156	10	167	155	156	7	4.5	17
	µg/l	D2M		1.22	147	10	156	146	146	8	5.6	17
	µg/l	N3M		-0.09	2749	10	2737	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		-1.35	0.065	25	0.054	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		-1.17	0.072	25	0.061	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		-0.79	0.17	20	0.157	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		0.52	88.0	10	90.3	87.5	87.6	3.2	3.7	16
	µg/l	D2M		0.92	13.1	10	13.7	13.1	13.1	0.6	4.2	16
	µg/l	N3M		0.77	182	10	189	182	183	7	3.6	19
Mo	µg/l	A1M		0.06	33.0	10	33.1	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-0.51	10.4	15	10.0	10.3	10.4	0.5	4.6	14
	µg/l	N3M		-0.60	20.1	10	19.5	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		0.11	9.50	15	9.6	9.4	9.5	0.4	3.8	14
	µg/l	D2M		-1.39	0.49	20	0.42	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-0.03	8.40	15	8.38	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-0.04	3.36	15	3.35	3.19	3.15	0.21	6.6	13
	µg/l	D2M		0.00	1.34	15	1.34	1.30	1.30	0.05	3.7	11
	µg/l	N3M		0.40	4.98	15	5.13	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-1.47	15.0	10	13.9	14.2	14.3	1.0	6.8	12
	µg/l	D2M		0.13	4.76	20	4.82	4.82	4.76	0.46	9.7	11
	µg/l	N3M		-0.15	9.77	20	9.62	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		0.81	9.90	15	10.50	10.00	9.90	0.40	4.1	9
	µg/l	D2M		0.09	5.34	20	5.39	5.32	5.34	0.42	8.0	10
	µg/l	N3M		0.17	1.43	25	1.46	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		-0.55	17.0	15	16.3	16.3	16.5	1.6	9.9	9
	µg/l	D2M		-0.21	5.06	15	4.98	5.02	5.06	0.27	5.2	8
	µg/l	N3M		-0.18	9.79	15	9.66	9.80	9.79	0.47	4.8	10
Sr	µg/l	A1M		-1.09	22.0	10	20.8	21.9	21.7	1.3	6.1	9
	µg/l	D2M		-0.76	40.1	15	37.8	40.2	40.1	2.3	5.8	9
	µg/l	N3M		-1.03	71.4	15	65.9	71.6	71.4	3.8	5.3	11
Stot	mg/l	A1M		-1.00	12.0	10	11.4	11.6	11.7	0.6	4.7	12
	mg/l	D2M		-0.61	7.92	10	7.68	7.95	7.92	0.23	2.9	9
	mg/l	N3M		-0.87	7.32	10	7.00	7.30	7.37	0.38	5.1	13
Ti	µg/l	A1M		-0.27	15.0	10	14.8	14.8	14.8	0.6	4.1	8
	µg/l	D2M		-0.37	6.57	10	6.45	6.55	6.57	0.20	3.1	6
	µg/l	N3M		-0.68	93.8	10	90.6	93.7	93.8	3.0	3.2	10
U	µg/l	A1M		0.22	4.20	15	4.27	4.35	4.35	0.27	6.3	10
	µg/l	D2M		-0.49	2.17	15	2.09	2.18	2.17	0.13	5.8	10
	µg/l	N3M		-0.55	1.21	15	1.16	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-1.43	5.60	10	5.20	5.38	5.33	0.22	4.2	13
	µg/l	D2M		-1.10	5.62	10	5.31	5.58	5.62	0.24	4.2	11
	µg/l	N3M		-1.17	5.46	10	5.14	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		-1.22	13.1	10	12.3	13.1	13.2	0.7	5.5	16
	µg/l	D2M		-0.28	14.3	15	14.0	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.66	24.1	15	22.9	23.8	24.2	1.3	5.6	19

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.38	320	10	326	322	317	18	5.7	15
	µg/l	D2M		0.44	44.7	15	46.2	45.3	44.8	2.5	5.7	16
	µg/l	N3M		0.10	2880	10	2895	2895	2900	123	4.2	17
Cd	µg/l	A1M		0.32	7.1	15	7.27	7.07	7.02	0.39	5.6	15
Cr	µg/l	A1M		-0.38	14.5	10	14.2	14.0	14.1	0.7	4.7	16
Cu	µg/l	A1M		0.61	23.3	10	24.0	23.0	22.8	0.9	4.1	16
	µg/l	N3M		1.10	22.8	10	24.1	22.6	22.7	0.7	3.2	20
Fe	µg/l	N3M		0.25	2749	10	2783	2737	2747	78	2.9	21
Mn	µg/l	D2M		0.50	13.1	10	13.4	13.1	13.1	0.6	4.2	16
Mo	µg/l	A1M		1.11	33.0	10	34.8	33.1	33.3	1.8	5.3	14
	µg/l	D2M		0.38	10.4	15	10.7	10.3	10.4	0.5	4.6	14
	µg/l	N3M		0.36	20.1	10	20.5	20.1	20.1	1.1	5.5	17
Stot	mg/l	D2M		21176.97	7.92	10	8394.00	7.95	7.92	0.23	2.9	9
	mg/l	N3M		20847.49	7.32	10	7637.50	7.30	7.37	0.38	5.1	13
Zn	µg/l	A1M		2.27	13.1	10	14.6	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.49	14.3	15	14.8	14.4	14.4	0.7	5.1	16
	µg/l	N3M		0.46	24.1	15	24.9	23.8	24.2	1.3	5.6	19

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.13	320	10	322	322	317	18	5.7	15
	µg/l	D2M		0.76	44.7	15	47.3	45.3	44.8	2.5	5.7	16
	µg/l	N3M		0.10	2880	10	2895	2895	2900	123	4.2	17
As	µg/l	A1M		0.66	6.50	15	6.8	6.2	6.3	0.6	9.3	13
	µg/l	D2M		1.50	0.35	15	0.39	0.35	0.35	0.03	7.5	10
	µg/l	N3M		-0.03	0.96	25	0.96	0.94	0.97	0.13	13.5	12
B	µg/l	A1M		-0.85	35.4	10	33.9	35.5	35.4	1.6	4.5	10
	µg/l	D2M		-0.10	10.3	10	10.3	10.3	10.3	0.4	3.7	7
	µg/l	N3M		-0.20	17.7	20	17.4	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		-0.78	18.0	10	17.3	17.4	17.5	0.5	2.7	11
	µg/l	D2M		-0.25	4.47	10	4.42	4.45	4.47	0.15	3.4	11
	µg/l	N3M		-0.54	55.4	10	53.9	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		1.32	7.1	15	7.81	7.07	7.02	0.39	5.6	15
	µg/l	D2M		1.59	0.42	15	0.47	0.42	0.41	0.02	4.9	13
	µg/l	N3M		1.55	0.62	15	0.69	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		1.24	5.10	10	5.42	4.93	4.99	0.23	4.6	13
	µg/l	D2M		1.76	0.55	15	0.62	0.55	0.55	0.01	2.5	10
	µg/l	N3M		1.46	1.87	15	2.08	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-0.83	14.5	10	13.9	14.0	14.1	0.7	4.7	16
	µg/l	D2M		0.34	5.31	10	5.40	5.32	5.30	0.18	3.5	14
	µg/l	N3M		0.16	6.89	10	6.95	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.26	23.3	10	23.0	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.49	349	10	358	350	349	10	3.0	16
	µg/l	N3M		0.53	22.8	10	23.4	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-0.26	156	10	154	155	156	7	4.5	17
	µg/l	D2M		0.75	147	10	153	146	146	8	5.6	17
	µg/l	N3M		-0.11	2749	10	2734	2737	2747	78	2.9	21

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Hg	µg/l	A1Hg		0.16	0.065	25	0.066	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		0.15	0.072	25	0.073	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		0.12	0.17	20	0.172	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		0.39	88.0	10	89.7	87.5	87.6	3.2	3.7	16
	µg/l	D2M		1.37	13.1	10	14.0	13.1	13.1	0.6	4.2	16
	µg/l	N3M		0.82	182	10	190	182	183	7	3.6	19
Mo	µg/l	A1M		1.00	33.0	10	34.7	33.1	33.3	1.8	5.3	14
	µg/l	D2M		0.32	10.4	15	10.7	10.3	10.4	0.5	4.6	14
	µg/l	N3M		0.50	20.1	10	20.6	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		0.98	9.50	15	10.2	9.4	9.5	0.4	3.8	14
	µg/l	D2M		0.60	0.49	20	0.52	0.50	0.49	0.04	7.1	11
	µg/l	N3M		1.17	8.40	15	9.14	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		0.56	3.36	15	3.50	3.19	3.15	0.21	6.6	13
	µg/l	D2M		0.40	1.34	15	1.38	1.30	1.30	0.05	3.7	11
	µg/l	N3M		0.44	4.98	15	5.15	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-1.07	15.0	10	14.2	14.2	14.3	1.0	6.8	12
	µg/l	D2M		0.26	4.76	20	4.89	4.82	4.76	0.46	9.7	11
	µg/l	N3M		0.17	9.77	20	9.94	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		0.24	9.90	15	10.08	10.00	9.90	0.40	4.1	9
	µg/l	D2M		0.48	5.34	20	5.60	5.32	5.34	0.42	8.0	10
	µg/l	N3M		1.45	1.43	25	1.69	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		-0.31	17.0	15	16.6	16.3	16.5	1.6	9.9	9
	µg/l	D2M		0.30	5.06	15	5.18	5.02	5.06	0.27	5.2	8
	µg/l	N3M		0.15	9.79	15	9.90	9.80	9.79	0.47	4.8	10
Sr	µg/l	A1M		0.00	22.0	10	22.0	21.9	21.7	1.3	6.1	9
	µg/l	D2M		0.37	40.1	15	41.2	40.2	40.1	2.3	5.8	9
	µg/l	N3M		0.03	71.4	15	71.6	71.6	71.4	3.8	5.3	11
Ti	µg/l	A1M		0.53	15.0	10	15.4	14.8	14.8	0.6	4.1	8
	µg/l	D2M		-0.50	6.57	10	6.41	6.55	6.57	0.20	3.1	6
	µg/l	N3M		-0.44	93.8	10	91.8	93.7	93.8	3.0	3.2	10
U	µg/l	A1M		1.89	4.20	15	4.80	4.35	4.35	0.27	6.3	10
	µg/l	D2M		1.08	2.17	15	2.35	2.18	2.17	0.13	5.8	10
	µg/l	N3M		0.72	1.21	15	1.28	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		0.45	5.60	10	5.73	5.38	5.33	0.22	4.2	13
	µg/l	D2M		1.60	5.62	10	6.07	5.58	5.62	0.24	4.2	11
	µg/l	N3M		1.12	5.46	10	5.77	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		-0.38	13.1	10	12.9	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.19	14.3	15	14.5	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.39	24.1	15	23.4	23.8	24.2	1.3	5.6	19

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.06	320	10	321	322	317	18	5.7	15
	µg/l	D2M		-0.33	44.7	15	43.6	45.3	44.8	2.5	5.7	16
	µg/l	N3M		0.63	2880	10	2970	2895	2900	123	4.2	17
As	µg/l	A1M		-0.70	6.50	15	6.2	6.2	6.3	0.6	9.3	13
	µg/l	D2M		-1.10	0.35	15	0.32	0.35	0.35	0.03	7.5	10
	µg/l	N3M		-1.09	0.96	25	0.83	0.94	0.97	0.13	13.5	12

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
B	µg/l	A1M		-0.06	35.4	10	35.3	35.5	35.4	1.6	4.5	10
	µg/l	D2M		-0.29	10.3	10	10.2	10.3	10.3	0.4	3.7	7
	µg/l	N3M		-0.17	17.7	20	17.4	17.6	17.7	1.8	9.9	10
Ba	µg/l	A1M		-0.72	18.0	10	17.4	17.4	17.5	0.5	2.7	11
	µg/l	D2M		-0.72	4.47	10	4.31	4.45	4.47	0.15	3.4	11
	µg/l	N3M		-0.79	55.4	10	53.2	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		-0.18	7.1	15	7.01	7.07	7.02	0.39	5.6	15
	µg/l	D2M		-0.08	0.42	15	0.42	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-0.06	0.62	15	0.62	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-1.06	5.10	10	4.83	4.93	4.99	0.23	4.6	13
	µg/l	D2M		-0.40	0.55	15	0.53	0.55	0.55	0.01	2.5	10
	µg/l	N3M		0.07	1.87	15	1.88	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		0.48	14.5	10	14.9	14.0	14.1	0.7	4.7	16
	µg/l	D2M		0.09	5.31	10	5.34	5.32	5.30	0.18	3.5	14
	µg/l	N3M		0.51	6.89	10	7.07	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-1.16	23.3	10	22.0	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.46	349	10	357	350	349	10	3.0	16
	µg/l	N3M		-1.14	22.8	10	21.5	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		0.58	156	10	161	155	156	7	4.5	17
	µg/l	D2M		-0.20	147	10	146	146	146	8	5.6	17
	µg/l	N3M		0.15	2749	10	2770	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		-2.77	0.065	25	0.043	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		-2.89	0.072	25	0.046	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		-0.59	0.17	20	0.160	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		0.45	88.0	10	90.0	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-1.07	13.1	10	12.4	13.1	13.1	0.6	4.2	16
	µg/l	N3M		0.49	182	10	187	182	183	7	3.6	19
Mo	µg/l	A1M		-0.42	33.0	10	32.3	33.1	33.3	1.8	5.3	14
	µg/l	D2M		-0.72	10.4	15	9.8	10.3	10.4	0.5	4.6	14
	µg/l	N3M		-1.19	20.1	10	18.9	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-0.69	9.50	15	9.0	9.4	9.5	0.4	3.8	14
	µg/l	D2M		-0.63	0.49	20	0.46	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-0.32	8.40	15	8.20	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-1.77	3.36	15	2.92	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.65	1.34	15	1.28	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.28	4.98	15	4.88	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-1.20	15.0	10	14.1	14.2	14.3	1.0	6.8	12
	µg/l	D2M		-0.85	4.76	20	4.36	4.82	4.76	0.46	9.7	11
	µg/l	N3M		-0.53	9.77	20	9.26	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		-0.49	9.90	15	9.54	10.00	9.90	0.40	4.1	9
	µg/l	D2M		-0.75	5.34	20	4.94	5.32	5.34	0.42	8.0	10
	µg/l	N3M		-1.06	1.43	25	1.24	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		2.63	17.0	15	20.4	16.3	16.5	1.6	9.9	9
	µg/l	D2M		-0.14	5.06	15	5.01	5.02	5.06	0.27	5.2	8
	µg/l	N3M		0.10	9.79	15	9.86	9.80	9.79	0.47	4.8	10
Sr	µg/l	A1M		-1.41	22.0	10	20.5	21.9	21.7	1.3	6.1	9
	µg/l	D2M		-1.00	40.1	15	37.1	40.2	40.1	2.3	5.8	9
	µg/l	N3M		-0.36	71.4	15	69.5	71.6	71.4	3.8	5.3	11

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Stot	mg/l	A1M		-0.33	12.0	10	11.8	11.6	11.7	0.6	4.7	12
	mg/l	D2M		0.54	7.92	10	8.14	7.95	7.92	0.23	2.9	9
	mg/l	N3M		0.53	7.32	10	7.52	7.30	7.37	0.38	5.1	13
Ti	µg/l	A1M		0.27	15.0	10	15.2	14.8	14.8	0.6	4.1	8
	µg/l	D2M		0.24	6.57	10	6.65	6.55	6.57	0.20	3.1	6
	µg/l	N3M		-0.19	93.8	10	92.9	93.7	93.8	3.0	3.2	10
U	µg/l	A1M		0.06	4.20	15	4.22	4.35	4.35	0.27	6.3	10
	µg/l	D2M		-0.49	2.17	15	2.09	2.18	2.17	0.13	5.8	10
	µg/l	N3M		-0.28	1.21	15	1.19	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-0.80	5.60	10	5.38	5.38	5.33	0.22	4.2	13
	µg/l	D2M		-0.87	5.62	10	5.38	5.58	5.62	0.24	4.2	11
	µg/l	N3M		-0.64	5.46	10	5.29	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		-1.07	13.1	10	12.4	13.1	13.2	0.7	5.5	16
	µg/l	D2M		-0.79	14.3	15	13.5	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.19	24.1	15	23.8	23.8	24.2	1.3	5.6	19

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-2.34	320	10	283	322	317	18	5.7	15
	µg/l	D2M		-0.43	44.7	15	43.3	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-19.98	2880	10	3	2895	2900	123	4.2	17
As	µg/l	A1M		-0.88	6.50	15	6.1	6.2	6.3	0.6	9.3	13
	µg/l	D2M		-0.17	0.35	15	0.35	0.35	0.35	0.03	7.5	10
	µg/l	N3M		-0.36	0.96	25	0.92	0.94	0.97	0.13	13.5	12
Ba	µg/l	A1M		-1.06	18.0	10	17.1	17.4	17.5	0.5	2.7	11
	µg/l	D2M		0.01	4.47	10	4.47	4.45	4.47	0.15	3.4	11
	µg/l	N3M		-0.07	55.4	10	55.2	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		-0.05	7.1	15	7.07	7.07	7.02	0.39	5.6	15
	µg/l	D2M		0.27	0.42	15	0.43	0.42	0.41	0.02	4.9	13
	µg/l	N3M		-0.22	0.62	15	0.61	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		-0.92	5.10	10	4.87	4.93	4.99	0.23	4.6	13
	µg/l	D2M		0.27	0.55	15	0.56	0.55	0.55	0.01	2.5	10
	µg/l	N3M		0.01	1.87	15	1.87	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		-1.79	14.5	10	13.2	14.0	14.1	0.7	4.7	16
	µg/l	D2M		-0.44	5.31	10	5.19	5.32	5.30	0.18	3.5	14
	µg/l	N3M		-0.67	6.89	10	6.66	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-1.03	23.3	10	22.1	23.0	22.8	0.9	4.1	16
	µg/l	D2M		-0.94	349	10	333	350	349	10	3.0	16
	µg/l	N3M		-0.37	22.8	10	22.4	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-0.78	156	10	150	155	156	7	4.5	17
	µg/l	D2M		-0.20	147	10	146	146	146	8	5.6	17
	µg/l	N3M		0.08	2749	10	2761	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		1.91	0.065	25	0.081	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		0.83	0.072	25	0.080	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		0.85	0.17	20	0.185	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-0.38	88.0	10	86.3	87.5	87.6	3.2	3.7	16
	µg/l	D2M		0.24	13.1	10	13.3	13.1	13.1	0.6	4.2	16
	µg/l	N3M		0.10	182	10	183	182	183	7	3.6	19

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Mo	µg/l	A1M		0.57	33.0	10	33.9	33.1	33.3	1.8	5.3	14
	µg/l	D2M		0.40	10.4	15	10.7	10.3	10.4	0.5	4.6	14
	µg/l	N3M		1.20	20.1	10	21.3	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-0.72	9.50	15	9.0	9.4	9.5	0.4	3.8	14
	µg/l	D2M		-0.12	0.49	20	0.48	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-0.06	8.40	15	8.36	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-0.93	3.36	15	3.13	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-0.63	1.34	15	1.28	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.55	4.98	15	4.77	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		0.86	15.0	10	15.6	14.2	14.3	1.0	6.8	12
	µg/l	D2M		1.55	4.76	20	5.50	4.82	4.76	0.46	9.7	11
	µg/l	N3M		1.38	9.77	20	11.12	9.83	9.75	0.80	8.2	13
Se	µg/l	A1M		-0.71	9.90	15	9.37	10.00	9.90	0.40	4.1	9
	µg/l	D2M		-0.03	5.34	20	5.32	5.32	5.34	0.42	8.0	10
	µg/l	N3M		0.32	1.43	25	1.49	1.42	1.46	0.22	15.2	12
Sn	µg/l	A1M		-0.29	17.0	15	16.6	16.3	16.5	1.6	9.9	9
	µg/l	D2M		0.82	5.06	15	5.37	5.02	5.06	0.27	5.2	8
	µg/l	N3M		0.76	9.79	15	10.35	9.80	9.79	0.47	4.8	10
Stot	mg/l	A1M		-0.07	12.0	10	12.0	11.6	11.7	0.6	4.7	12
	mg/l	D2M		0.68	7.92	10	8.19	7.95	7.92	0.23	2.9	9
	mg/l	N3M		0.58	7.32	10	7.53	7.30	7.37	0.38	5.1	13
U	µg/l	A1M		1.26	4.20	15	4.60	4.35	4.35	0.27	6.3	10
	µg/l	D2M		1.08	2.17	15	2.35	2.18	2.17	0.13	5.8	10
	µg/l	N3M		0.81	1.21	15	1.28	1.23	1.21	0.07	6.0	11
V	µg/l	A1M		-0.54	5.60	10	5.45	5.38	5.33	0.22	4.2	13
	µg/l	D2M		0.64	5.62	10	5.80	5.58	5.62	0.24	4.2	11
	µg/l	N3M		0.56	5.46	10	5.61	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		0.04	13.1	10	13.1	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.84	14.3	15	15.2	14.4	14.4	0.7	5.1	16
	µg/l	N3M		0.59	24.1	15	25.2	23.8	24.2	1.3	5.6	19

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
As	µg/l	N3M		61.83	0.96	25	8.38	0.94	0.97	0.13	13.5	12
Cd	µg/l	N3M		-1.18	0.62	15	0.57	0.62	0.62	0.04	6.0	15
Co	µg/l	N3M		-0.93	1.87	15	1.74	1.88	1.87	0.13	6.9	15
Cr	µg/l	N3M		-0.38	6.89	10	6.76	6.76	6.82	0.26	3.8	17
Cu	µg/l	N3M		-0.40	22.8	10	22.3	22.6	22.7	0.7	3.2	20
Fe	µg/l	N3M		1.02	2749	10	2889	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		0.68	0.065	25	0.071	0.068	0.069	0.014	19.7	12
	µg/l	N3Hg		0.76	0.17	20	0.183	0.173	0.173	0.016	9.6	15
Mn	µg/l	N3M		-0.28	182	10	179	182	183	7	3.6	19
Mo	µg/l	N3M		-0.53	20.1	10	19.6	20.1	20.1	1.1	5.5	17
Ni	µg/l	N3M		-0.79	8.40	15	7.91	8.38	8.41	0.37	4.4	17
Pb	µg/l	N3M		-0.33	4.98	15	4.86	4.90	4.95	0.15	3.0	14
Sb	µg/l	N3M		-1.23	9.77	20	8.57	9.83	9.75	0.80	8.2	13
Se	µg/l	N3M		-0.42	1.43	25	1.36	1.42	1.46	0.22	15.2	12
Sn	µg/l	N3M		-0.10	9.79	15	9.72	9.80	9.79	0.47	4.8	10

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Sr	µg/l	N3M		-0.73	71.4	15	67.5	71.6	71.4	3.8	5.3	11
Ti	µg/l	N3M		0.16	93.8	10	94.5	93.7	93.8	3.0	3.2	10
V	µg/l	N3M		-0.55	5.46	10	5.31	5.35	5.46	0.25	4.5	15
Zn	µg/l	N3M		-1.54	24.1	15	21.3	23.8	24.2	1.3	5.6	19

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.22	320	10	324	322	317	18	5.7	15
	µg/l	D2M		0.76	44.7	15	47.3	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-1.15	2880	10	2715	2895	2900	123	4.2	17
As	µg/l	A1M		0.07	6.50	15	6.5	6.2	6.3	0.6	9.3	13
	µg/l	D2M		0.42	0.35	15	0.36	0.35	0.35	0.03	7.5	10
	µg/l	N3M		2.21	0.96	25	1.23	0.94	0.97	0.13	13.5	12
Ba	µg/l	A1M		-0.67	18.0	10	17.4	17.4	17.5	0.5	2.7	11
	µg/l	D2M		-0.11	4.47	10	4.45	4.45	4.47	0.15	3.4	11
	µg/l	N3M		0.36	55.4	10	56.4	54.7	55.6	2.5	4.6	14
Cd	µg/l	A1M		0.08	7.1	15	7.15	7.07	7.02	0.39	5.6	15
	µg/l	D2M		0.54	0.42	15	0.44	0.42	0.41	0.02	4.9	13
	µg/l	N3M		0.39	0.62	15	0.64	0.62	0.62	0.04	6.0	15
Co	µg/l	A1M		0.12	5.10	10	5.13	4.93	4.99	0.23	4.6	13
	µg/l	D2M		0.18	0.55	15	0.56	0.55	0.55	0.01	2.5	10
	µg/l	N3M		0.36	1.87	15	1.92	1.88	1.87	0.13	6.9	15
Cr	µg/l	A1M		0.00	14.5	10	14.5	14.0	14.1	0.7	4.7	16
	µg/l	D2M		0.56	5.31	10	5.46	5.32	5.30	0.18	3.5	14
	µg/l	N3M		0.64	6.89	10	7.11	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		-0.04	23.3	10	23.3	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.66	349	10	361	350	349	10	3.0	16
	µg/l	N3M		-0.31	22.8	10	22.5	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		0.32	156	10	159	155	156	7	4.5	17
	µg/l	D2M		1.29	147	10	157	146	146	8	5.6	17
	µg/l	N3M		0.77	2749	10	2855	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		-0.18	0.065	25	0.064	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		-0.56	0.072	25	0.067	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		-0.59	0.17	20	0.160	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		0.77	88.0	10	91.4	87.5	87.6	3.2	3.7	16
	µg/l	D2M		0.38	13.1	10	13.4	13.1	13.1	0.6	4.2	16
	µg/l	N3M		0.60	182	10	188	182	183	7	3.6	19
Mo	µg/l	A1M		2.67	33.0	10	37.4	33.1	33.3	1.8	5.3	14
	µg/l	D2M		1.22	10.4	15	11.4	10.3	10.4	0.5	4.6	14
	µg/l	N3M		2.19	20.1	10	22.3	20.1	20.1	1.1	5.5	17
Ni	µg/l	A1M		-0.01	9.50	15	9.5	9.4	9.5	0.4	3.8	14
	µg/l	D2M		0.17	0.49	20	0.50	0.50	0.49	0.04	7.1	11
	µg/l	N3M		0.53	8.40	15	8.74	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-0.67	3.36	15	3.19	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-1.04	1.34	15	1.24	1.30	1.30	0.05	3.7	11
	µg/l	N3M		-0.43	4.98	15	4.82	4.90	4.95	0.15	3.0	14
Sb	µg/l	A1M		-13.21	15.0	10	5.1	14.2	14.3	1.0	6.8	12
	µg/l	D2M		-6.45	4.76	20	1.69	4.82	4.76	0.46	9.7	11
	µg/l	N3M		-6.73	9.77	20	3.19	9.83	9.75	0.80	8.2	13

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Sr	µg/l	A1M		1.09	22.0	10	23.2	21.9	21.7	1.3	6.1	9
	µg/l	D2M		1.15	40.1	15	43.6	40.2	40.1	2.3	5.8	9
	µg/l	N3M		0.88	71.4	15	76.1	71.6	71.4	3.8	5.3	11
Stot	mg/l	A1M		0.25	12.0	10	12.2	11.6	11.7	0.6	4.7	12
	mg/l	D2M		2.92	7.92	10	9.08	7.95	7.92	0.23	2.9	9
	mg/l	N3M		1.86	7.32	10	8.00	7.30	7.37	0.38	5.1	13
V	µg/l	A1M		-0.07	5.60	10	5.58	5.38	5.33	0.22	4.2	13
	µg/l	D2M		6.23	5.62	10	7.37	5.58	5.62	0.24	4.2	11
	µg/l	N3M		0.86	5.46	10	5.70	5.35	5.46	0.25	4.5	15
Zn	µg/l	A1M		0.15	13.1	10	13.2	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.23	14.3	15	14.6	14.4	14.4	0.7	5.1	16
	µg/l	N3M		0.58	24.1	15	25.2	23.8	24.2	1.3	5.6	19

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		-2.53	320	10	280	322	317	18	5.7	15
	µg/l	D2M		-1.88	44.7	15	38.4	45.3	44.8	2.5	5.7	16
	µg/l	N3M		2.26	2880	10	3205	2895	2900	123	4.2	17
As	µg/l	A1M		2.30	6.50	15	7.6	6.2	6.3	0.6	9.3	13
	µg/l	D2M			0.35	15	*<2*	0.35	0.35	0.03	7.5	10
	µg/l	N3M			0.96	25	*<2*	0.94	0.97	0.13	13.5	12
Cd	µg/l	A1M		5.31	7.1	15	9.93	7.07	7.02	0.39	5.6	15
	µg/l	D2M		0.02	0.42	15	0.42	0.42	0.41	0.02	4.9	13
	µg/l	N3M		0.90	0.62	15	0.66	0.62	0.62	0.04	6.0	15
Cr	µg/l	A1M		1.43	14.5	10	15.5	14.0	14.1	0.7	4.7	16
	µg/l	D2M		-0.30	5.31	10	5.23	5.32	5.30	0.18	3.5	14
	µg/l	N3M		1.79	6.89	10	7.51	6.76	6.82	0.26	3.8	17
Cu	µg/l	A1M		2.66	23.3	10	26.4	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.15	349	10	352	350	349	10	3.0	16
	µg/l	N3M		4.04	22.8	10	27.4	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		-0.18	156	10	155	155	156	7	4.5	17
	µg/l	D2M		-2.03	147	10	132	146	146	8	5.6	17
	µg/l	N3M		-0.67	2749	10	2657	2737	2747	78	2.9	21
Hg	µg/l	A1Hg		2.65	0.065	25	0.087	0.068	0.069	0.014	19.7	12
	µg/l	D2Hg		1.94	0.072	25	0.090	0.076	0.073	0.014	18.6	12
	µg/l	N3Hg		1.24	0.17	20	0.191	0.173	0.173	0.016	9.6	15
Mn	µg/l	A1M		-1.82	88.0	10	80.0	87.5	87.6	3.2	3.7	16
	µg/l	D2M			13.1	10	*<10*	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-0.36	182	10	179	182	183	7	3.6	19
Ni	µg/l	A1M		-0.69	9.50	15	9.0	9.4	9.5	0.4	3.8	14
	µg/l	D2M			0.49	20	*<5*	0.50	0.49	0.04	7.1	11
	µg/l	N3M		-0.63	8.40	15	8.00	8.38	8.41	0.37	4.4	17
Pb	µg/l	A1M		-2.02	3.36	15	2.85	3.19	3.15	0.21	6.6	13
	µg/l	D2M		-2.64	1.34	15	1.08	1.30	1.30	0.05	3.7	11
	µg/l	N3M		0.33	4.98	15	5.11	4.90	4.95	0.15	3.0	14
Zn	µg/l	A1M		1.22	13.1	10	13.9	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.09	14.3	15	14.4	14.4	14.4	0.7	5.1	16
	µg/l	N3M		0.17	24.1	15	24.4	23.8	24.2	1.3	5.6	19

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Al	µg/l	A1M		0.38	320	10	326	322	317	18	5.7	15
	µg/l	D2M		-0.63	44.7	15	42.6	45.3	44.8	2.5	5.7	16
	µg/l	N3M		-0.29	2880	10	2839	2895	2900	123	4.2	17
Cu	µg/l	A1M		0.82	23.3	10	24.3	23.0	22.8	0.9	4.1	16
	µg/l	D2M		0.00	349	10	349	350	349	10	3.0	16
	µg/l	N3M		0.96	22.8	10	23.9	22.6	22.7	0.7	3.2	20
Fe	µg/l	A1M		0.00	156	10	156	155	156	7	4.5	17
	µg/l	D2M		-0.07	147	10	147	146	146	8	5.6	17
	µg/l	N3M		0.23	2749	10	2780	2737	2747	78	2.9	21
Mn	µg/l	A1M		0.02	88.0	10	88.1	87.5	87.6	3.2	3.7	16
	µg/l	D2M		-0.23	13.1	10	13.0	13.1	13.1	0.6	4.2	16
	µg/l	N3M		-0.22	182	10	180	182	183	7	3.6	19
Ni	µg/l	A1M		0.66	9.50	15	10.0	9.4	9.5	0.4	3.8	14
	µg/l	N3M		-0.71	8.40	15	7.96	8.38	8.41	0.37	4.4	17
Stot	mg/l	A1M		-1.25	12.0	10	11.3	11.6	11.7	0.6	4.7	12
	mg/l	D2M		0.16	7.92	10	7.99	7.95	7.92	0.23	2.9	9
	mg/l	N3M		-0.40	7.32	10	7.18	7.30	7.37	0.38	5.1	13
Zn	µg/l	A1M		0.38	13.1	10	13.4	13.1	13.2	0.7	5.5	16
	µg/l	D2M		0.19	14.3	15	14.5	14.4	14.4	0.7	5.1	16
	µg/l	N3M		-0.41	24.1	15	23.4	23.8	24.2	1.3	5.6	19

APPENDIX 8: Summary of the z scores

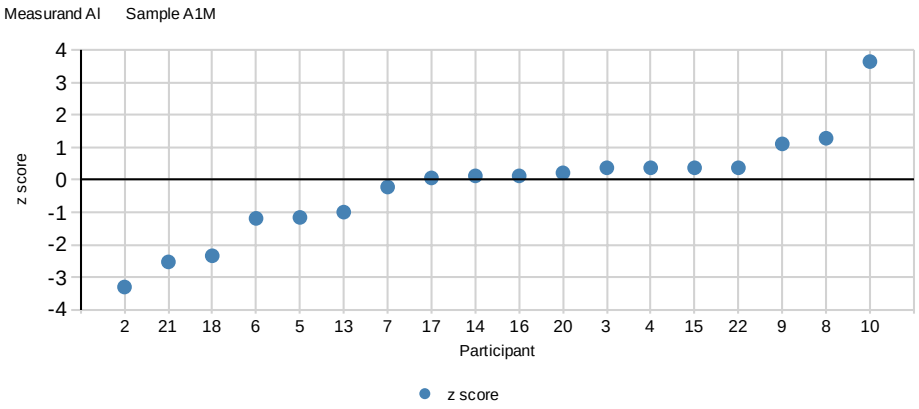
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Al	A1M	.	u	S	S	S	S	S	S	S	U	.	.	S	S	S	S	S	q	.	S	q	S	.	77.8
	D2M	.	u	S	S	S	S	S	S	.	S	.	.	S	S	S	S	S	S	.	S	S	S	.	94.1
	N3M	.	u	S	S	S	S	S	S	S	S	.	S	q	S	S	S	S	u	.	S	Q	S	.	78.9
As	A1M	.	S	S	S	S	S	.	q	.	S	.	.	.	S	.	S	S	S	.	S	Q	.	.	84.6
	D2M	.	.	S	S	S	S	.	S	.	U	.	.	.	S	.	S	S	S	.	S	.	.	.	90.9
	N3M	.	U	S	S	S	S	.	S	.	S	.	S	.	S	.	S	S	S	U	Q	.	.	.	78.6
B	A1M	.	.	S	S	S	S	S	S	S	U	.	.	.	S	.	S	S	.	.	.	.	.	.	90.9
	D2M	.	.	S	S	q	S	.	S	.	U	.	.	.	S	.	S	S	.	.	.	.	.	.	77.8
	N3M	.	.	S	S	S	S	.	S	S	U	.	Q	.	S	.	S	S	.	.	.	.	.	.	81.8
Ba	A1M	.	.	S	S	S	S	U	S	S	S	.	.	.	S	.	S	S	S	.	S	.	.	.	92.3
	D2M	.	.	S	S	S	S	U	S	.	S	.	.	.	S	.	S	S	S	.	S	.	.	.	91.7
	N3M	.	.	S	S	S	S	S	S	S	S	.	S	.	S	.	S	S	S	.	S	.	.	.	100
Cd	A1M	.	S	S	S	S	S	S	S	S	S	.	.	S	S	S	S	S	S	.	S	U	.	.	94.1
	D2M	.	U	S	S	S	S	.	S	.	U	.	.	S	S	.	S	S	S	.	S	S	.	.	85.7
	N3M	.	U	S	S	S	S	U	S	S	U	.	S	S	S	.	S	S	S	S	S	S	.	.	83.3
Co	A1M	.	.	S	S	S	S	S	S	S	S	.	.	.	S	.	S	S	S	.	S	.	.	.	100
	D2M	.	.	S	S	S	S	.	S	.	S	.	.	.	S	.	S	S	S	.	S	.	.	.	100
	N3M	.	.	S	S	S	S	S	S	S	S	.	S	.	S	.	S	S	S	S	S	.	.	.	100
Cr	A1M	.	S	S	S	S	S	S	q	S	S	.	.	.	S	S	S	S	S	.	S	S	.	.	93.8
	D2M	.	S	S	S	S	S	S	S	.	S	.	.	.	S	.	S	S	S	.	S	S	.	.	100
	N3M	.	S	S	S	S	S	S	S	S	S	.	U	.	S	.	S	S	S	S	S	S	.	.	94.1
Cu	A1M	.	S	S	S	S	S	S	q	S	S	.	.	S	S	S	S	S	S	.	S	Q	S	.	88.9
	D2M	.	S	S	S	S	S	S	S	.	S	.	.	S	S	.	S	S	S	.	S	S	S	.	100
	N3M	.	S	S	S	S	S	S	S	S	S	.	S	S	S	S	S	S	S	S	S	U	S	.	95.0
Fe	A1M	S	S	S	S	S	S	S	S	S	S	.	.	S	S	.	S	S	S	.	S	S	S	.	100
	D2M	S	q	S	S	S	S	S	S	.	S	.	.	S	S	.	S	S	S	.	S	q	S	.	88.2
	N3M	S	S	S	S	S	S	S	S	S	S	.	Q	S	S	S	S	S	S	S	S	S	S	.	95.2
Hg	A1Hg	.	S	S	.	U	S	.	U	.	S	.	.	.	S	.	S	q	S	S	S	Q	.	.	69.2
	D2Hg	.	Q	S	.	S	S	.	S	.	S	.	.	.	S	.	S	q	S	.	S	S	.	.	83.3
	N3Hg	.	S	S	S	S	S	.	S	.	S	.	S	.	S	.	S	S	S	S	S	S	.	.	100
Mn	A1M	.	S	S	S	S	S	S	S	S	S	.	.	S	S	.	S	S	S	.	S	S	S	.	100
	D2M	.	S	S	S	S	S	S	S	.	S	.	.	S	S	S	S	S	S	.	S	.	S	.	100
	N3M	.	S	S	S	S	S	S	S	S	S	.	S	S	S	.	S	S	S	S	S	S	S	.	100
Mo	A1M	.	.	S	S	S	S	S	S	S	S	.	.	S	S	S	S	S	S	.	Q	.	.	.	93.3
	D2M	.	.	S	S	S	S	q	S	.	U	.	.	S	S	S	S	S	S	.	S	.	.	.	85.7
	N3M	.	.	S	S	S	S	S	S	S	S	.	S	S	S	S	S	S	S	S	Q	.	.	.	94.1
Ni	A1M	.	S	S	S	S	S	S	q	S	S	.	.	.	S	.	S	S	S	.	S	S	S	.	93.8
	D2M	.	u	S	S	S	S	.	S	.	S	.	.	.	S	.	S	S	S	.	S	.	.	.	91.7
	N3M	.	u	S	S	S	S	S	S	S	S	.	S	.	S	.	S	S	S	S	S	S	S	.	94.4
Pb	A1M	.	q	S	S	S	S	.	S	.	S	.	.	S	S	.	S	S	S	.	S	q	.	.	85.7
	D2M	.	q	S	S	S	S	.	S	.	S	.	.	S	S	.	S	S	S	.	S	q	.	.	85.7
	N3M	.	S	S	S	S	S	.	S	Q	S	.	S	S	S	.	S	S	S	S	S	S	.	.	94.1
Sb	A1M	.	.	S	S	S	S	u	u	S	S	.	.	.	S	.	S	S	S	.	u	.	.	.	76.9
	D2M	.	.	S	S	S	S	S	S	.	S	.	.	.	S	.	S	S	S	.	u	.	.	.	91.7
	N3M	.	.	S	S	S	S	q	S	S	S	.	S	.	S	.	S	S	S	S	u	.	.	.	86.7

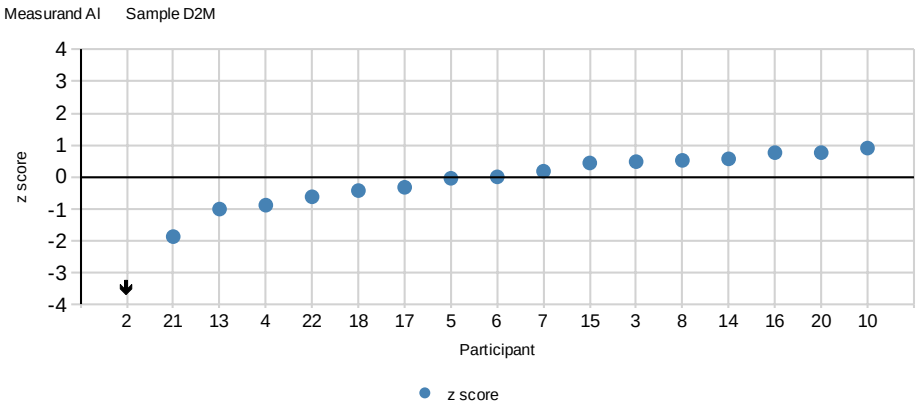
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Se	A1M	.	.	S	S	S	S	*u*	q	.	S	.	.	.	S	.	S	S	S	.	.	.	.	.	81.8
	D2M	.	.	S	S	S	S	.	S	.	S	.	.	.	S	.	S	S	S	.	.	.	.	.	100
	N3M	.	.	S	S	S	S	.	U	.	S	.	S	.	S	.	S	S	S	S	.	.	.	.	91.7
Sn	A1M	.	.	.	S	S	*S*	.	S	.	*S*	.	.	.	S	.	*S*	Q	*S*	.	.	.	.	.	88.9
	D2M	.	.	.	S	S	*S*	.	S	.	.	.	.	.	S	.	*S*	S	S	.	.	.	.	.	100
	N3M	.	.	.	S	S	*S*	.	S	.	.	.	S	.	S	.	*S*	S	*S*	S	.	.	.	.	100
Sr	A1M	.	.	.	S	*S*	S	.	S	.	*S*	.	.	.	S	.	*S*	S	.	.	*S*	.	.	.	100
	D2M	.	.	.	S	*S*	S	.	S	.	*S*	.	.	.	S	.	*S*	S	.	.	*S*	.	.	.	100
	N3M	.	.	.	S	*S*	S	.	S	.	*S*	.	S	.	S	.	*S*	S	.	S	*S*	.	.	.	100
Stot	A1M	.	.	.	S	*q*	S	S	S	S	*S*	.	.	.	S	.	.	S	S	.	*S*	.	*S*	.	91.7
	D2M	.	.	.	S	*S*	S	S	S	.	*Q*	.	.	.	S	U	.	S	S	.	*Q*	.	*S*	.	75.0
	N3M	.	.	.	S	*S*	S	S	S	S	*Q*	.	S	.	S	*U*	.	S	S	.	*S*	.	*S*	.	85.7
Ti	A1M	.	.	.	.	*S*	*S*	.	S	*S*	*S*	.	.	.	S	.	S	S	.	.	.	.	.	.	100
	D2M	.	.	.	.	*S*	*S*	.	U	.	*S*	.	.	.	S	.	*S*	S	.	.	.	.	.	.	85.7
	N3M	.	.	.	*S*	*S*	*S*	.	S	*S*	*S*	.	.	.	S	.	*S*	S	.	S	.	.	.	.	100
U	A1M	.	.	S	S	S	S	.	S	.	S	.	.	.	S	.	S	S	S	.	.	.	.	.	100
	D2M	.	.	S	S	S	S	.	S	.	S	.	.	.	S	.	S	S	S	.	.	.	.	.	100
	N3M	.	.	S	S	S	S	.	S	.	S	.	S	.	S	.	S	S	S	.	.	.	.	.	100
V	A1M	.	.	S	S	S	S	*q*	q	*S*	S	.	.	.	S	.	S	S	S	.	S	.	.	.	84.6
	D2M	.	.	S	S	S	S	*S*	S	.	S	.	.	.	S	.	S	S	S	.	U	.	.	.	91.7
	N3M	.	.	S	S	S	S	*S*	S	*S*	S	.	S	.	S	.	S	S	S	S	S	.	.	.	100
Zn	A1M	.	.	S	S	S	S	Q	S	S	S	.	.	S	S	*Q*	S	S	S	.	S	S	S	.	88.2
	D2M	.	.	S	S	S	S	S	S	.	S	.	.	S	S	*S*	S	S	S	.	S	S	S	.	100
	N3M	.	.	S	S	S	S	S	S	S	S	.	S	S	S	*S*	S	S	S	S	S	S	S	.	100
%		100	59	100	100	96	100	78	86	97	85		86	96	100	82	100	96	97	95	85	66	100		
accredited			23	54	65	60	64	29	70	21	54		22	24	70	1	57	70	58	19	33	29	17		

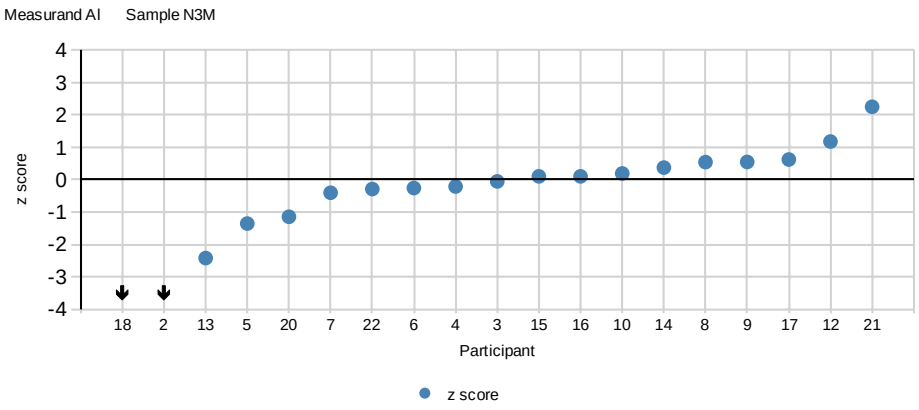
S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - other
% - percentage of satisfactory results

Totally satisfactory, % in all: 92 % in accredited: 94 % in non-accredited: 81

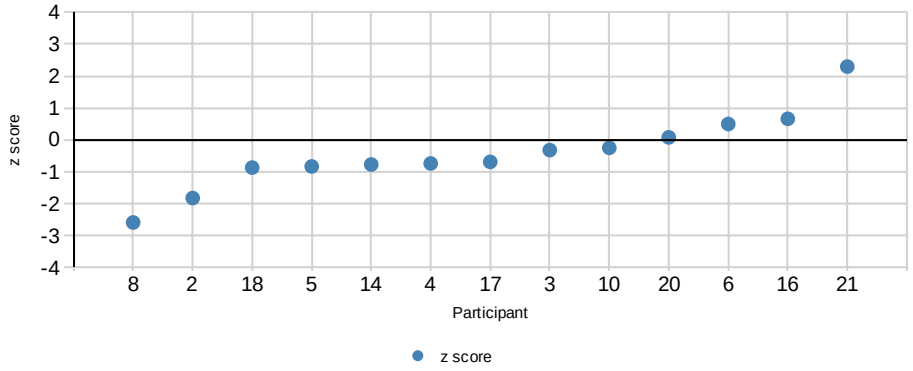
APPENDIX 9: z scores in ascending order



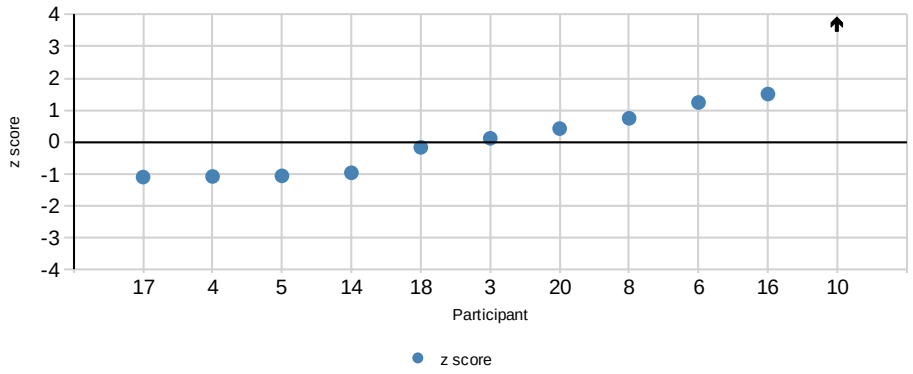




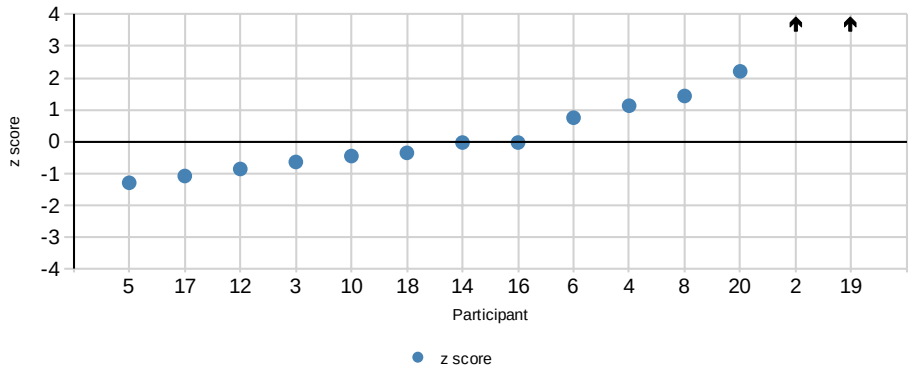
Measurand As Sample A1M

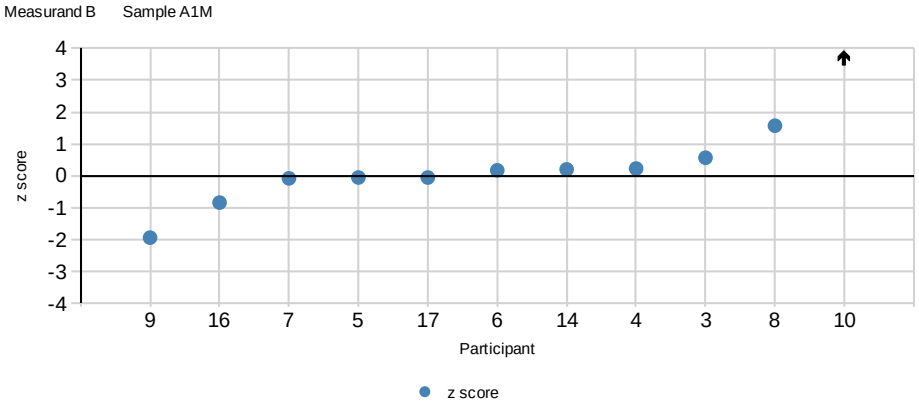


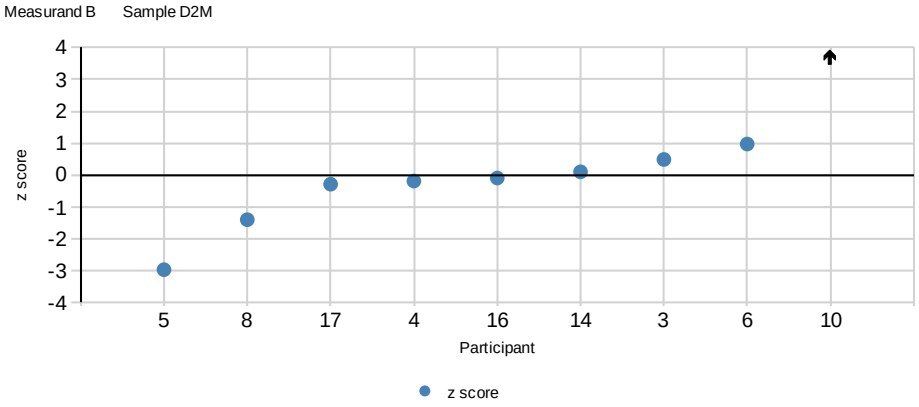
Measurand As Sample D2M

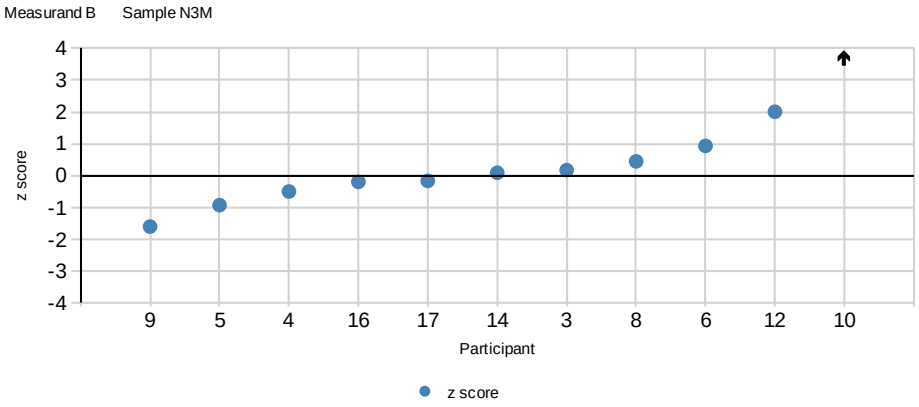


Measurand As Sample N3M

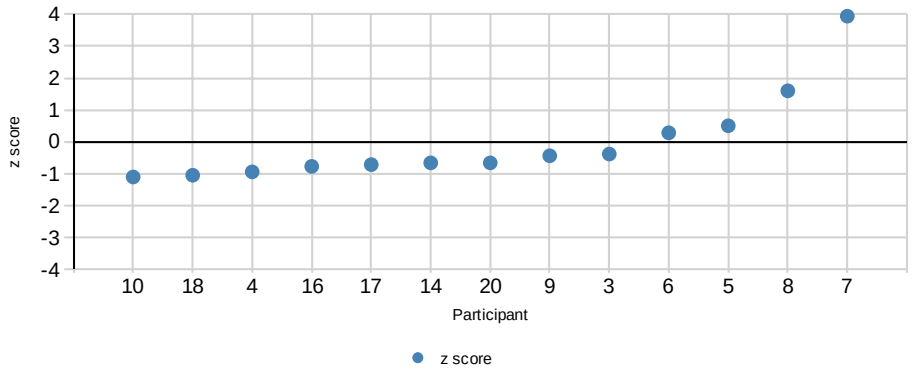



Measurand B Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
9 16 7 5 17 6 14 4 3 8 10
Participant
z score

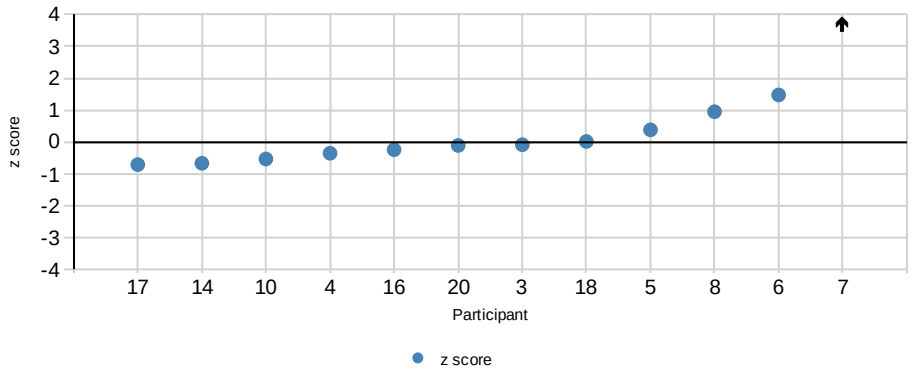

Measurand B Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 8 17 4 16 14 3 6 10
Participant
z score


Measurand B Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
9 5 4 16 17 14 3 8 6 12 10
Participant
z score

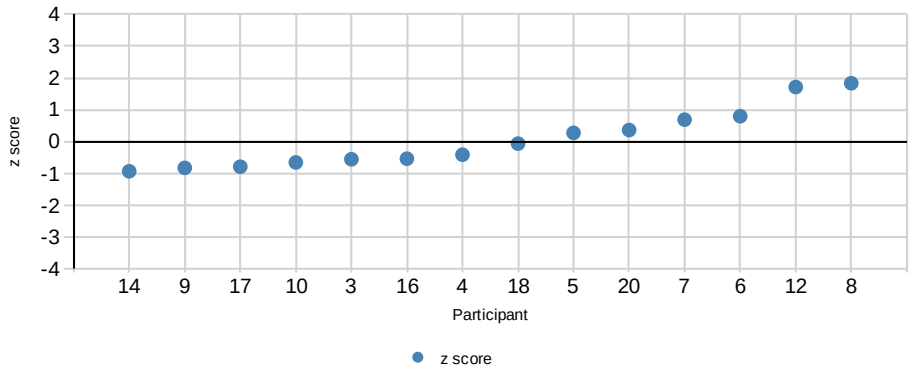
Measurand Ba Sample A1M

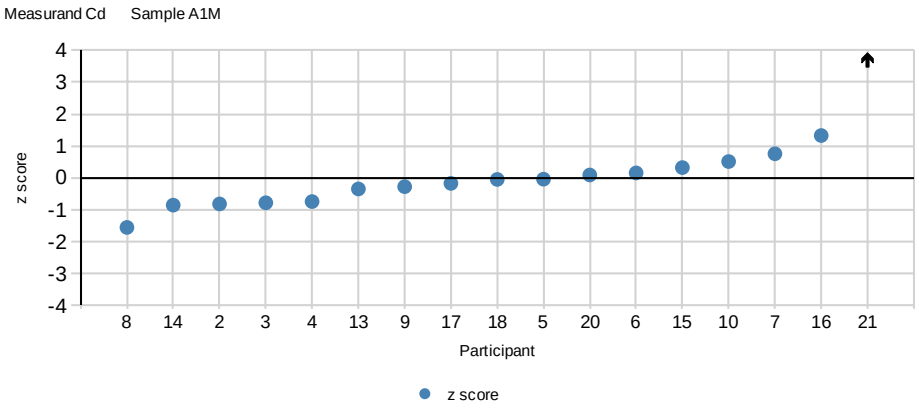


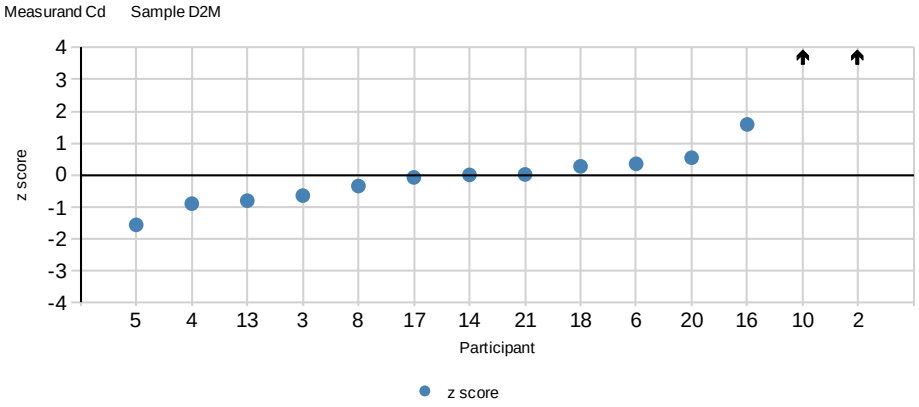
Measurand Ba Sample D2M

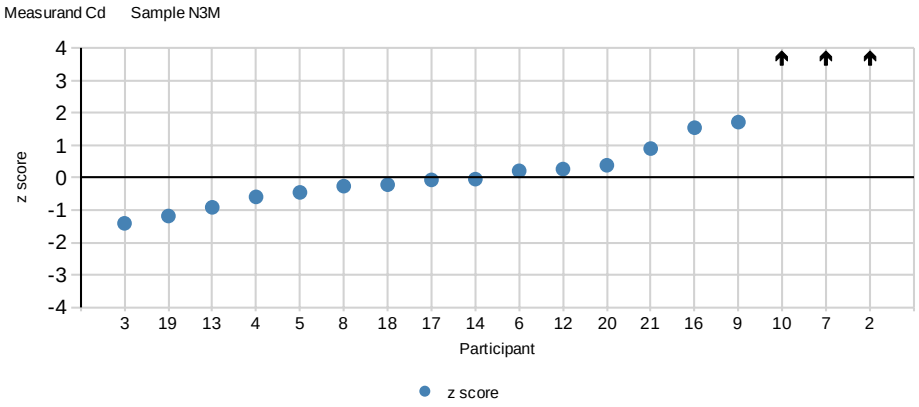


Measurand Ba Sample N3M

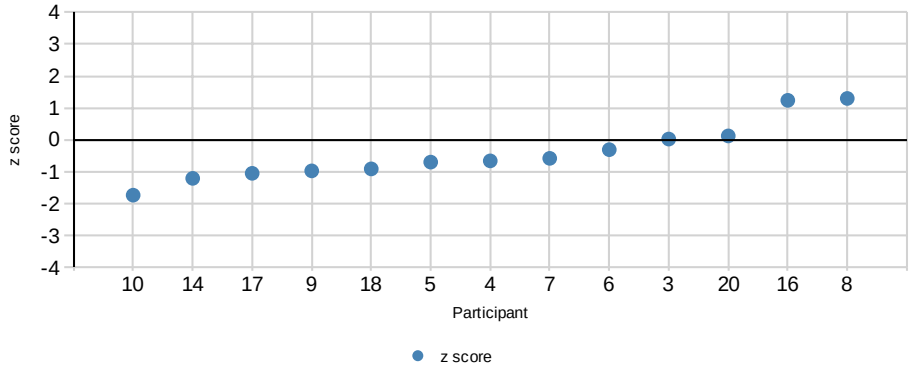



Measurand Cd Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
8 14 2 3 4 13 9 17 18 5 20 6 15 10 7 16 21
Participant
z score

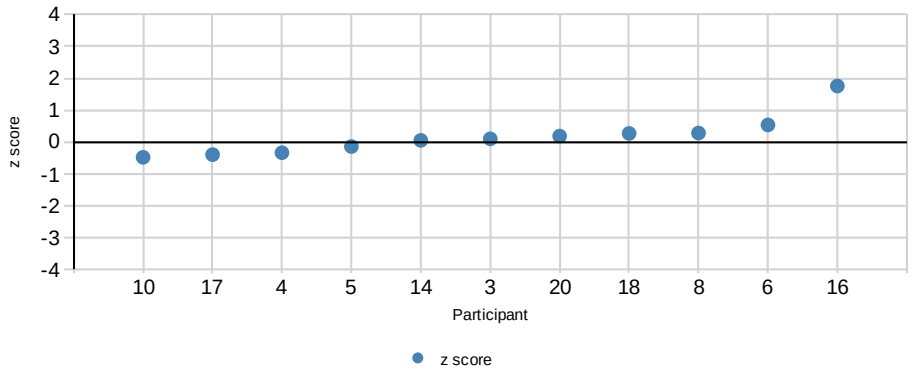

Measurand Cd Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 4 13 3 8 17 14 21 18 6 20 16 10 2
Participant
z score


Measurand Cd Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
3 19 13 4 5 8 18 17 14 6 12 20 21 16 9 10 7 2
Participant
z score

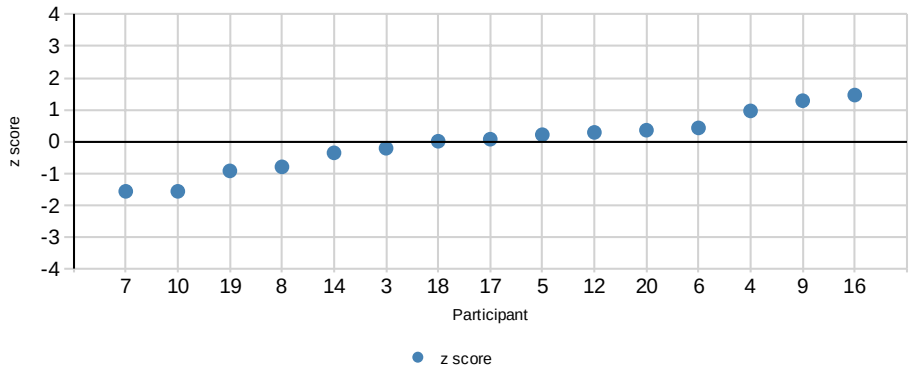
Measurand Co Sample A1M

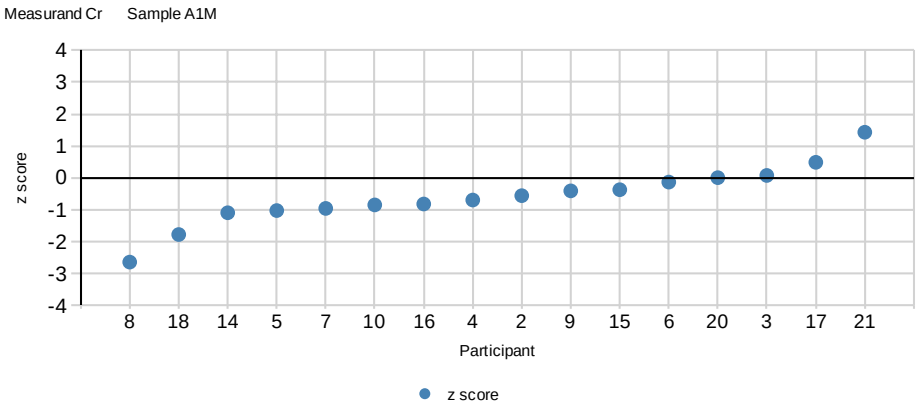


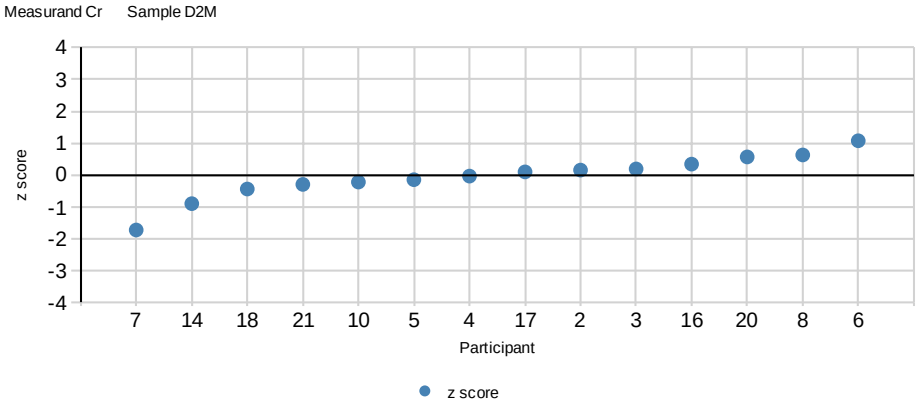
Measurand Co Sample D2M

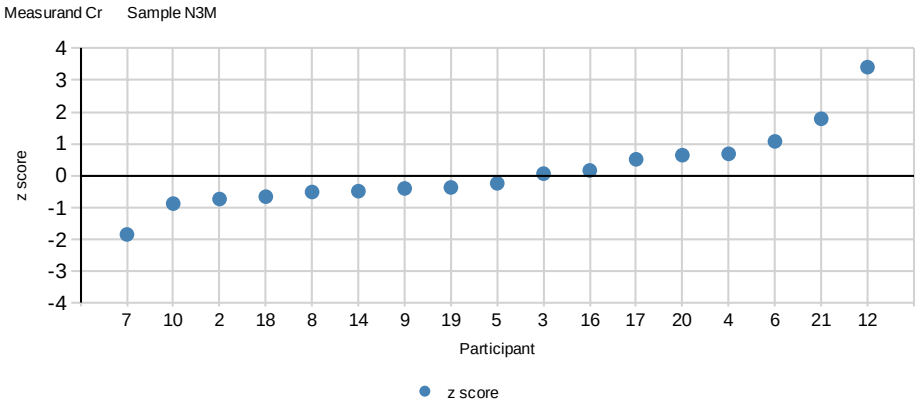


Measurand Co Sample N3M

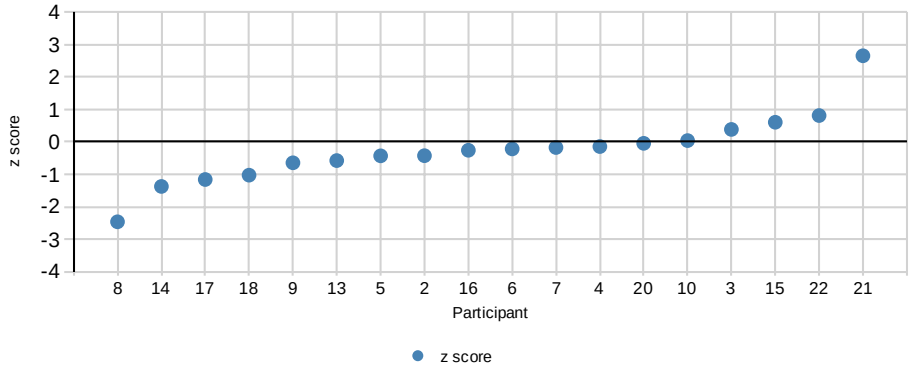



Measurand Cr Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
8 18 14 5 7 10 16 4 2 9 15 6 20 3 17 21
Participant
z score

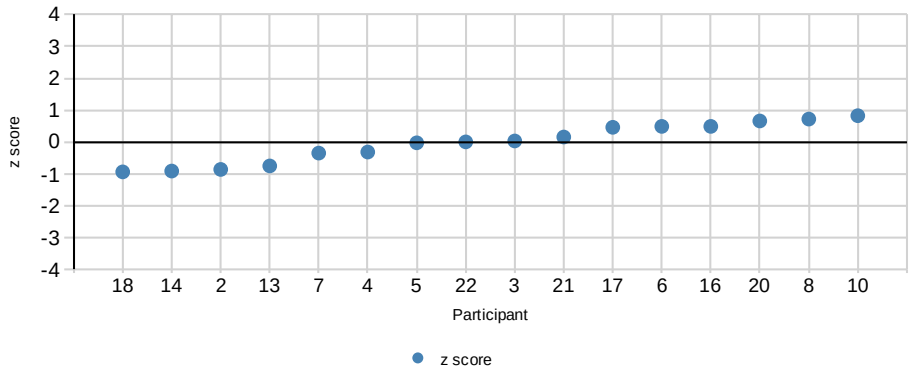

Measurand Cr Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
7 14 18 21 10 5 4 17 2 3 16 20 8 6
Participant
z score


Measurand Cr Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
7 10 2 18 8 14 9 19 5 3 16 17 20 4 6 21 12
Participant
z score

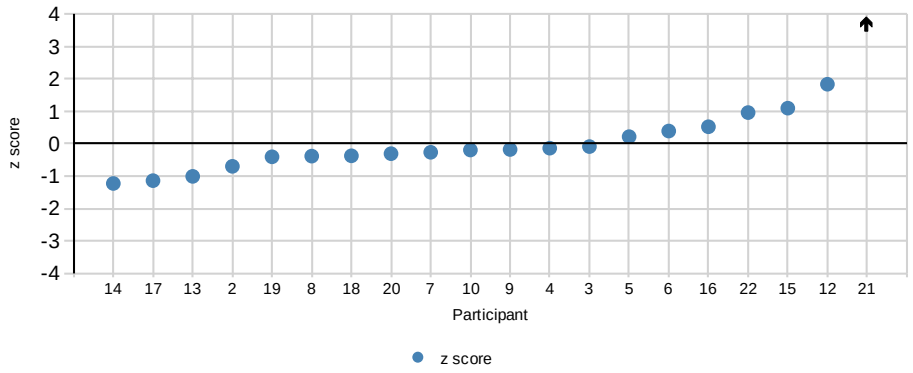
Measurand Cu Sample A1M

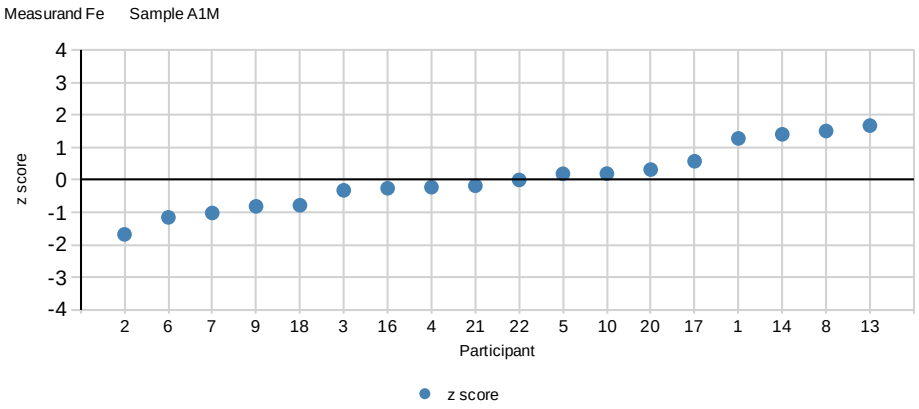


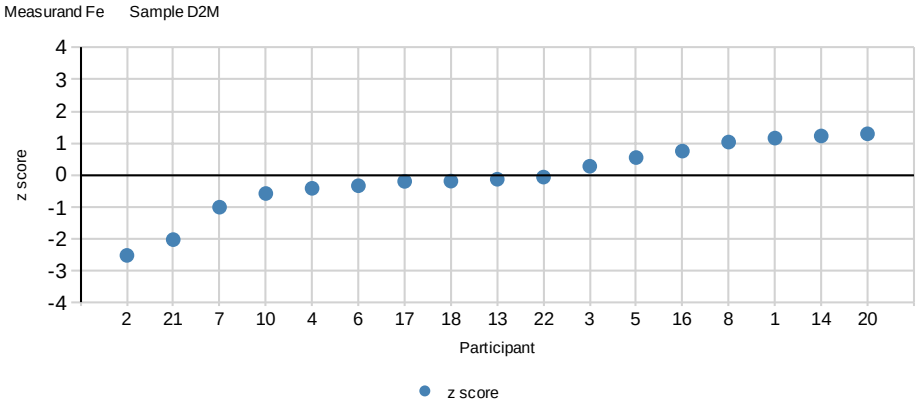
Measurand Cu Sample D2M

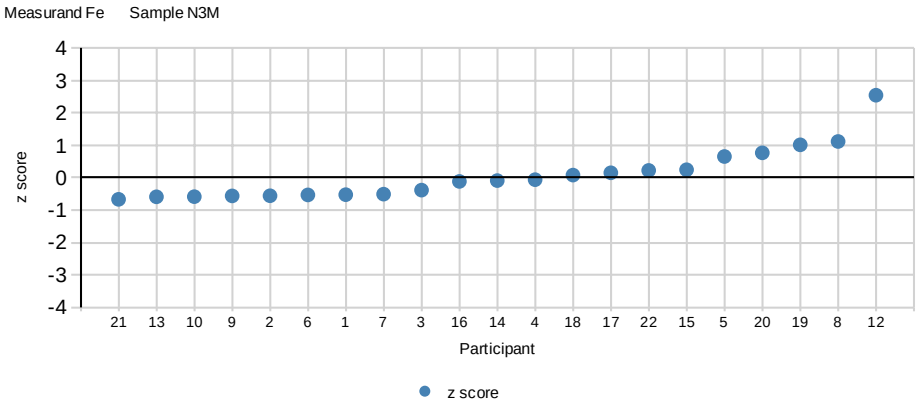


Measurand Cu Sample N3M

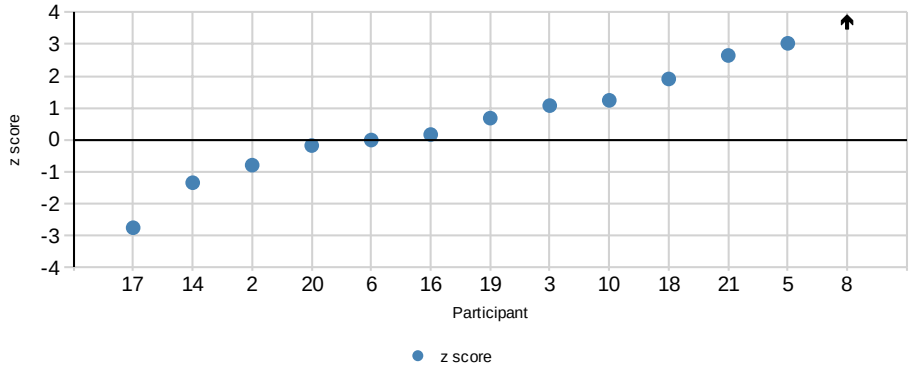



Measurand Fe Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
2 6 7 9 18 3 16 4 21 22 5 10 20 17 1 14 8 13
Participant
z score

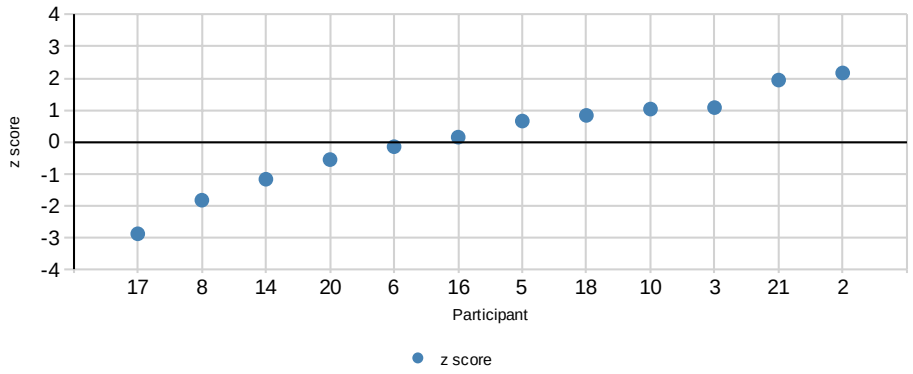

Measurand Fe Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
2 21 7 10 4 6 17 18 13 22 3 5 16 8 1 14 20
Participant
z score


Measurand Fe Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
21 13 10 9 2 6 1 7 3 16 14 4 18 17 22 15 5 20 19 8 12
Participant
z score

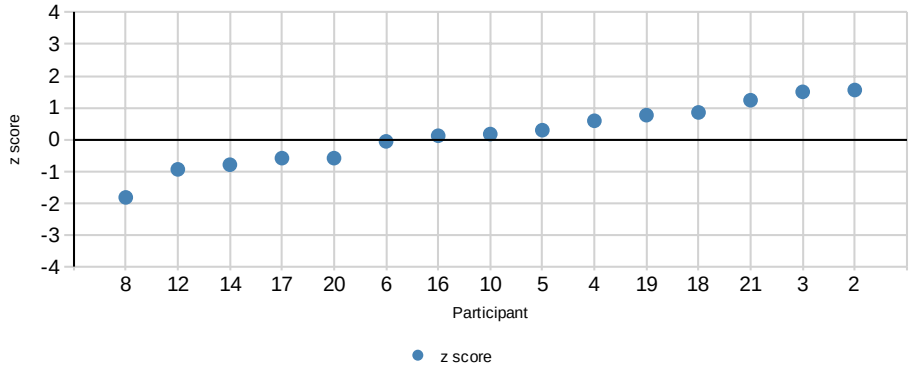
Measurand Hg Sample A1Hg

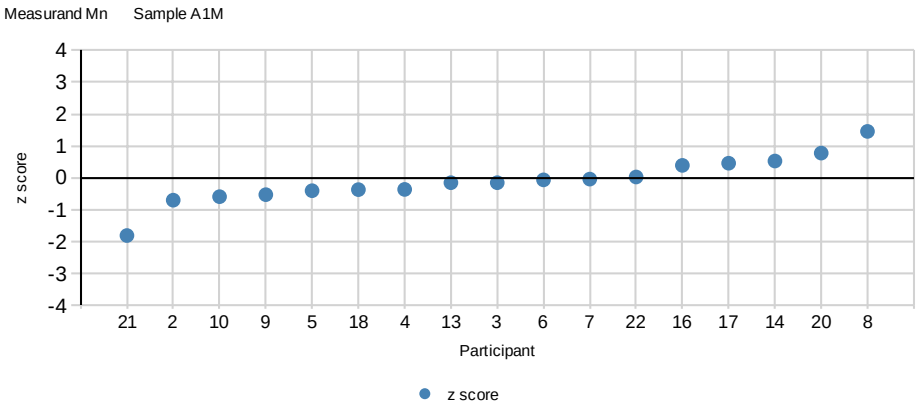


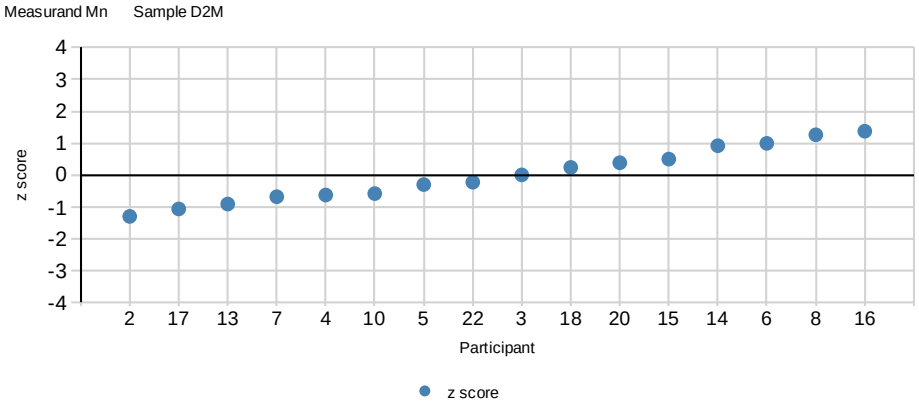
Measurand Hg Sample D2Hg

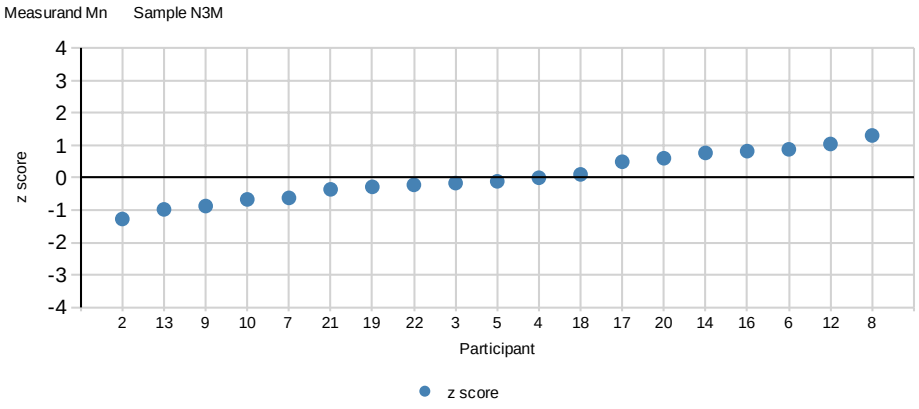


Measurand Hg Sample N3Hg

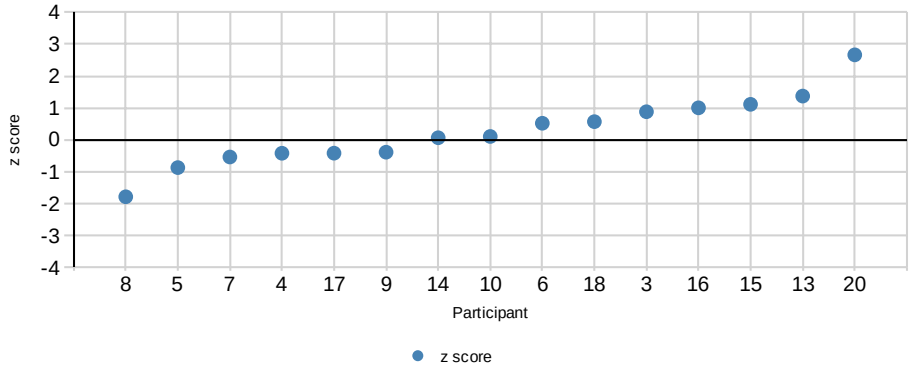



Measurand Mn Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
21 2 10 9 5 18 4 13 3 6 7 22 16 17 14 20 8
Participant
z score

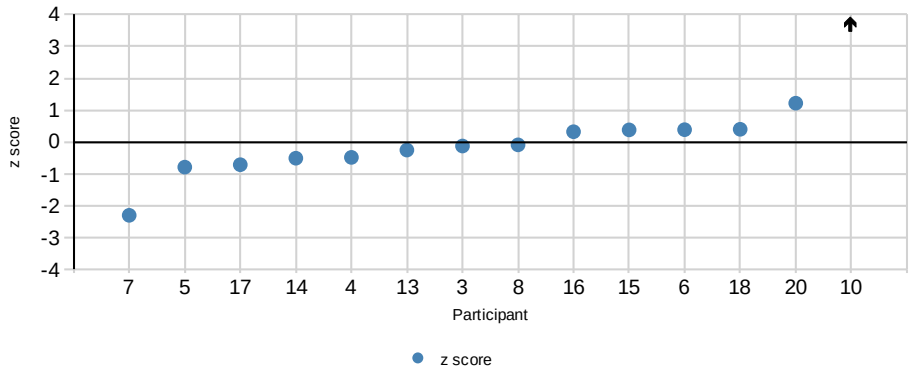

Measurand Mn Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
2 17 13 7 4 10 5 22 3 18 20 15 14 6 8 16
Participant
z score


Measurand Mn Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
2 13 9 10 7 21 19 22 3 5 4 18 17 20 14 16 6 12 8
Participant
z score

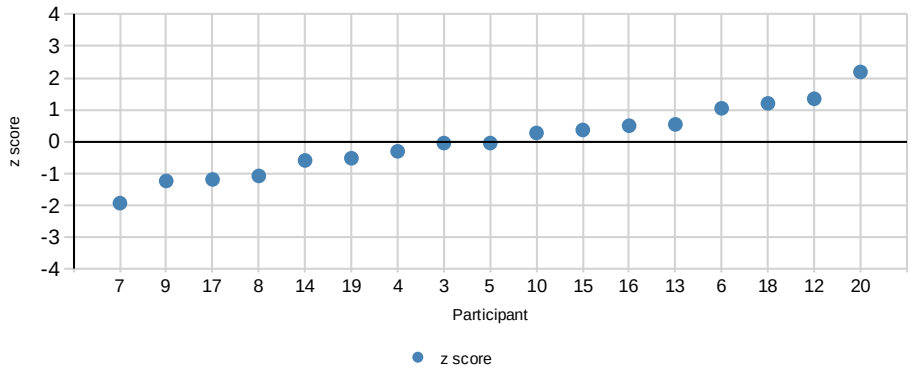
Measurand Mo Sample A1M

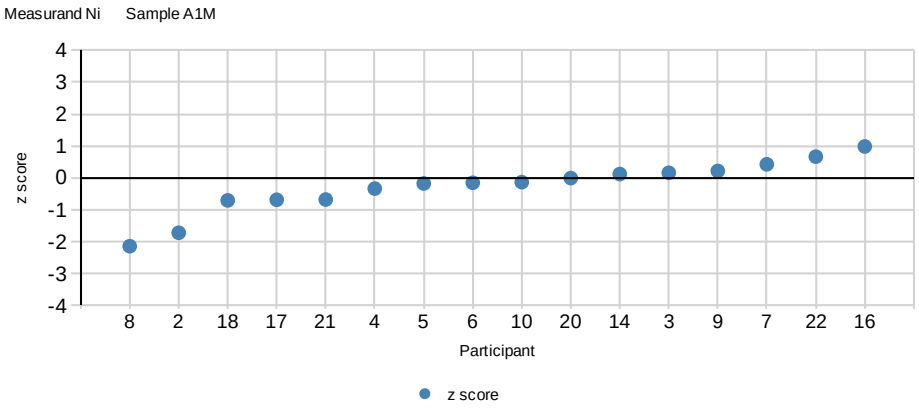


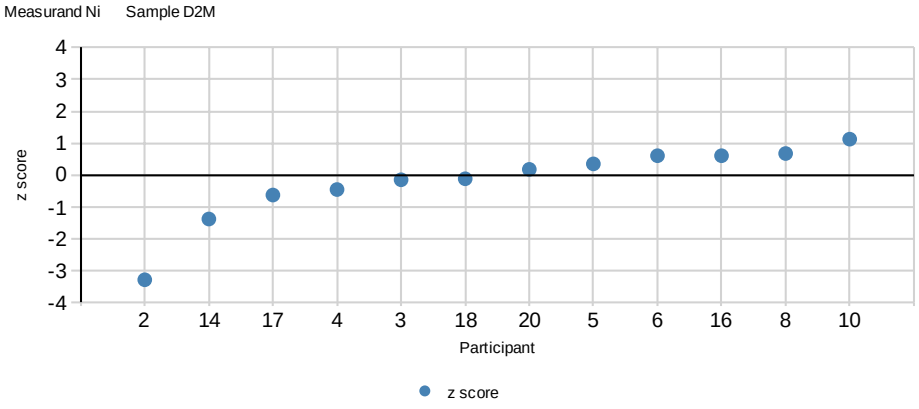
Measurand Mo Sample D2M

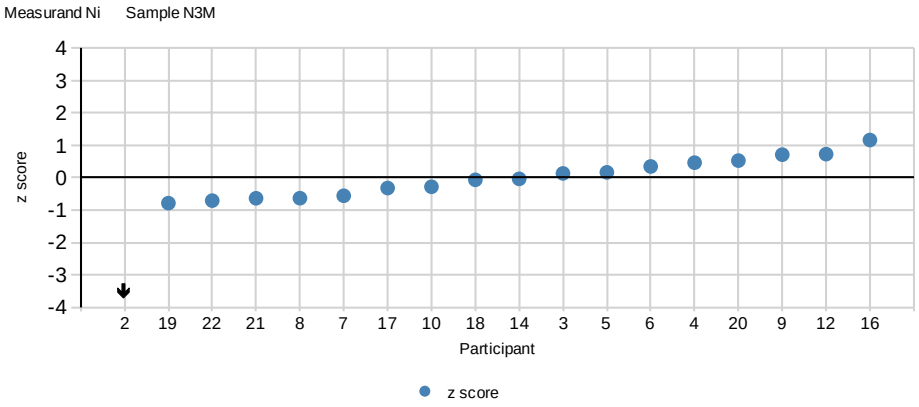


Measurand Mo Sample N3M

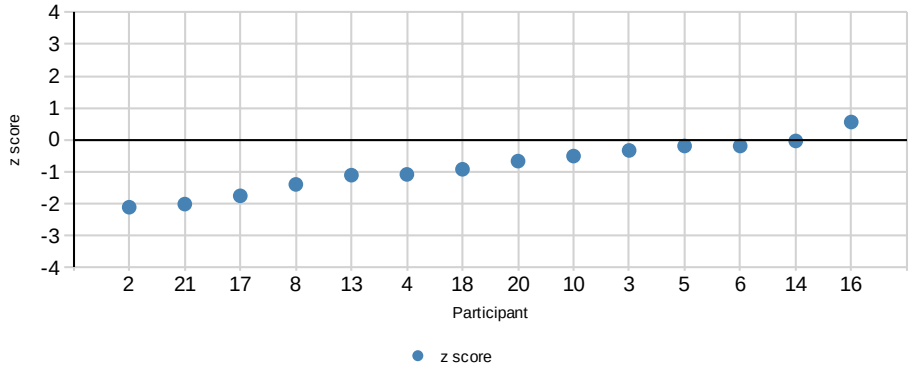



Measurand Ni Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
8 2 18 17 21 4 5 6 10 20 14 3 9 7 22 16
Participant
z score

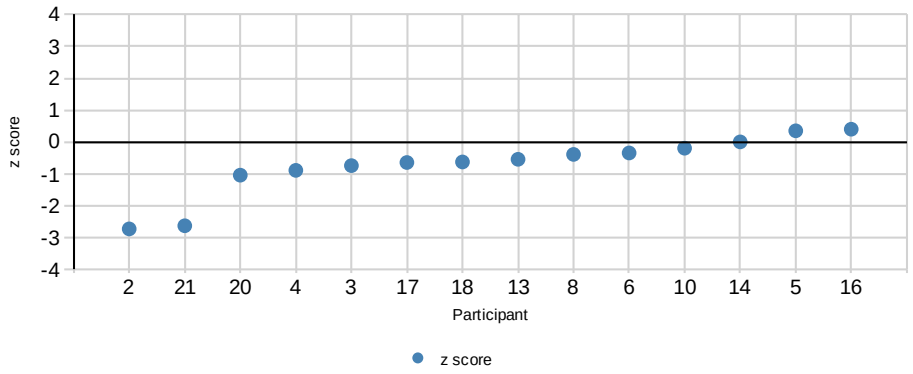

Measurand Ni Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
2 14 17 4 3 18 20 5 6 16 8 10
Participant
z score


Measurand Ni Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
2 19 22 21 8 7 17 10 18 14 3 5 6 4 20 9 12 16
Participant
z score

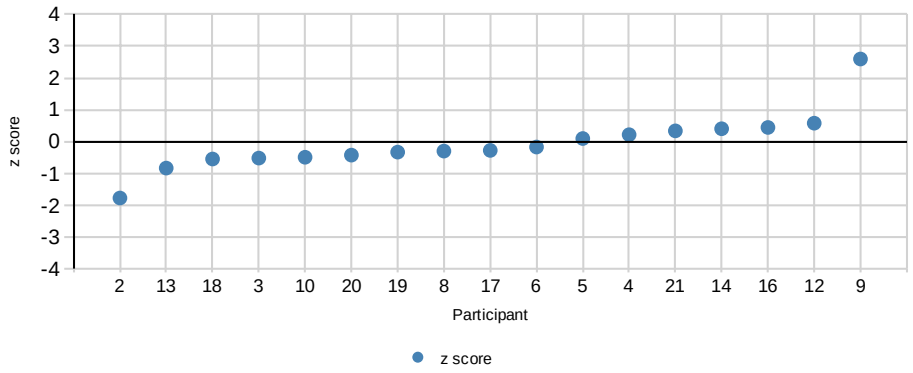
Measurand Pb Sample A1M

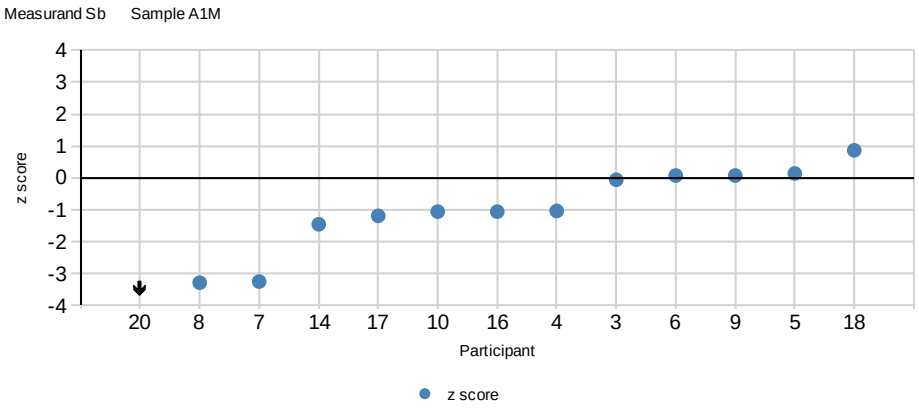


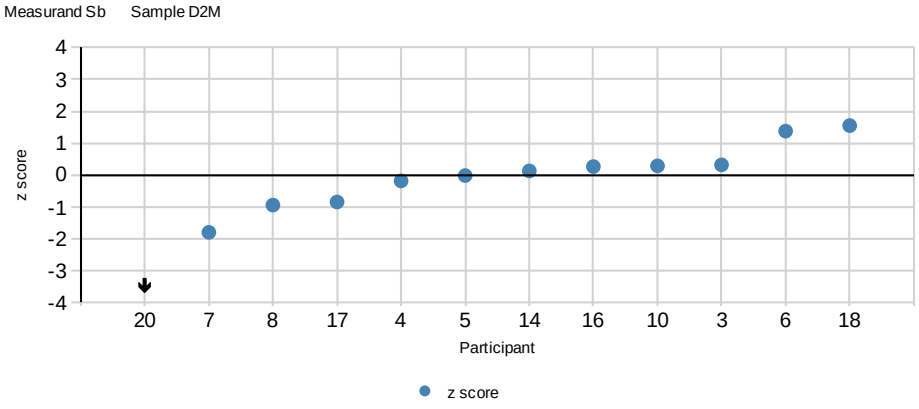
Measurand Pb Sample D2M

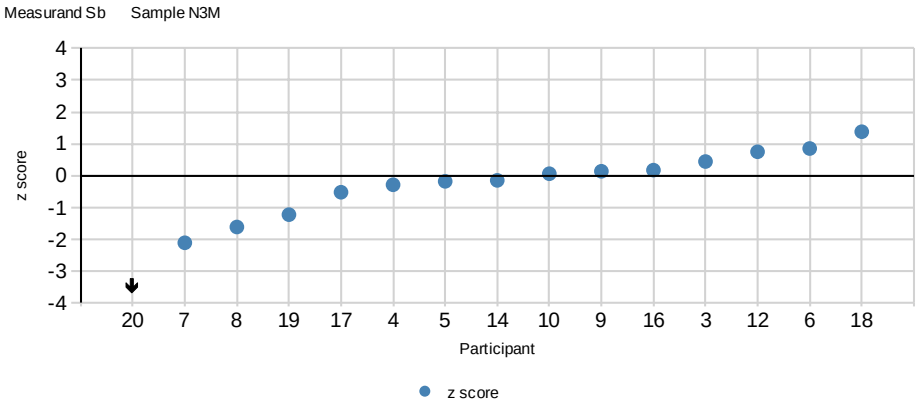


Measurand Pb Sample N3M

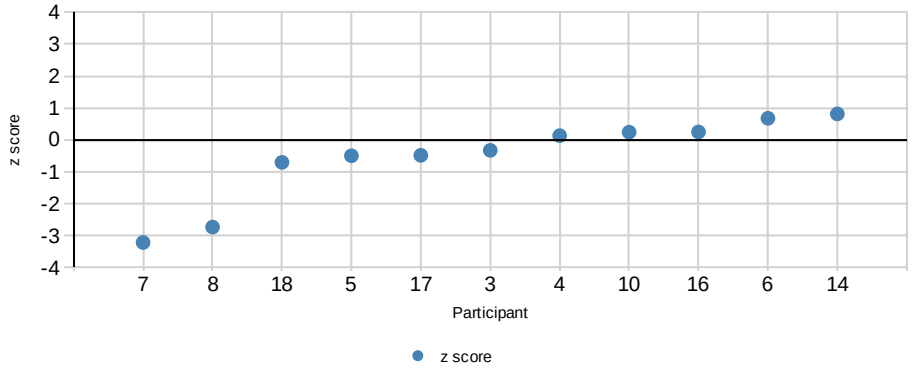



Measurand Sb Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
20 8 7 14 17 10 16 4 3 6 9 5 18
Participant
z score

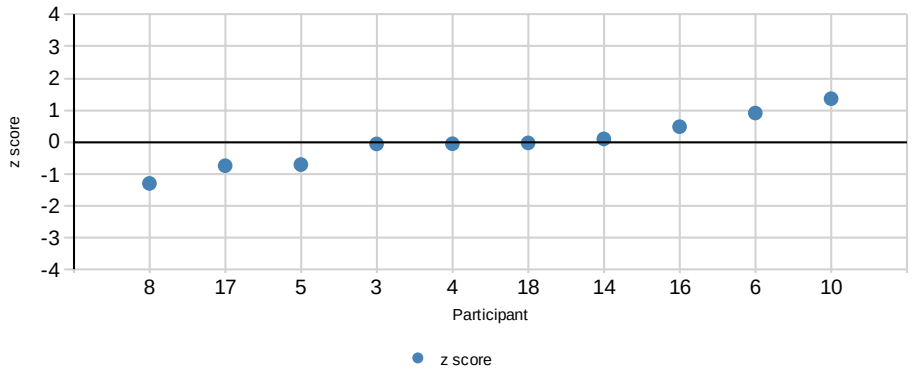

Measurand Sb Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
20 7 8 17 4 5 14 16 10 3 6 18
Participant
z score


Measurand Sb Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
20 7 8 19 17 4 5 14 10 9 16 3 12 6 18
Participant
z score

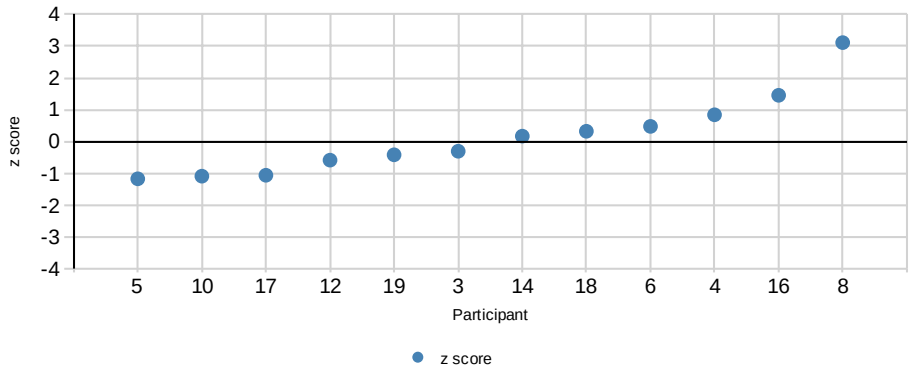
Measurand Se Sample A1M

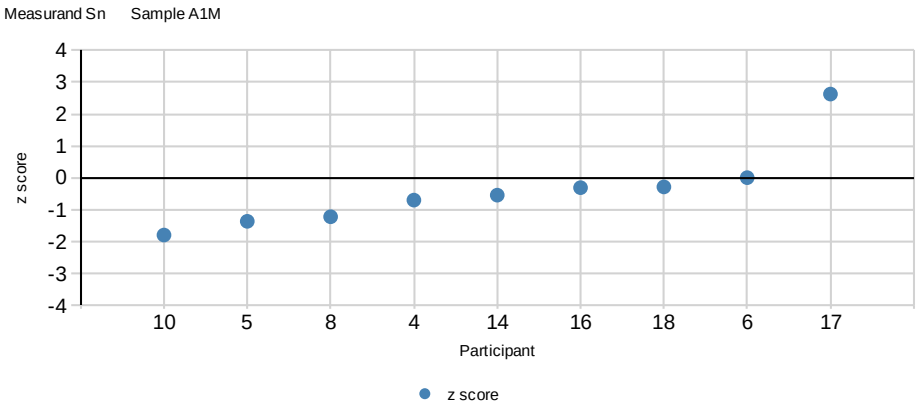


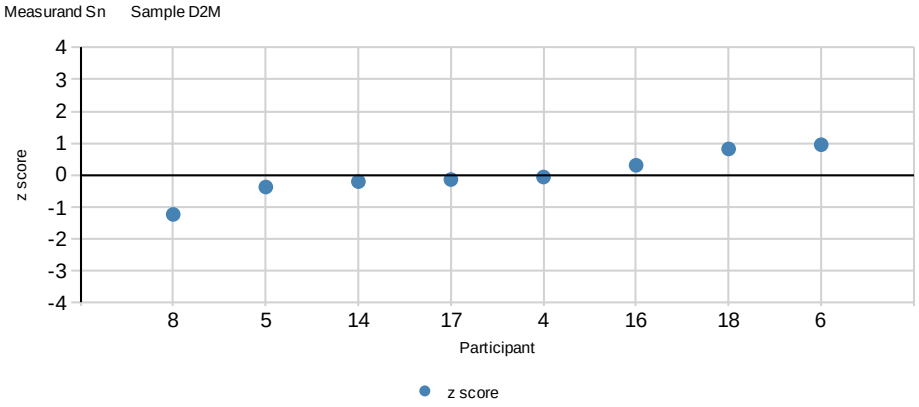
Measurand Se Sample D2M

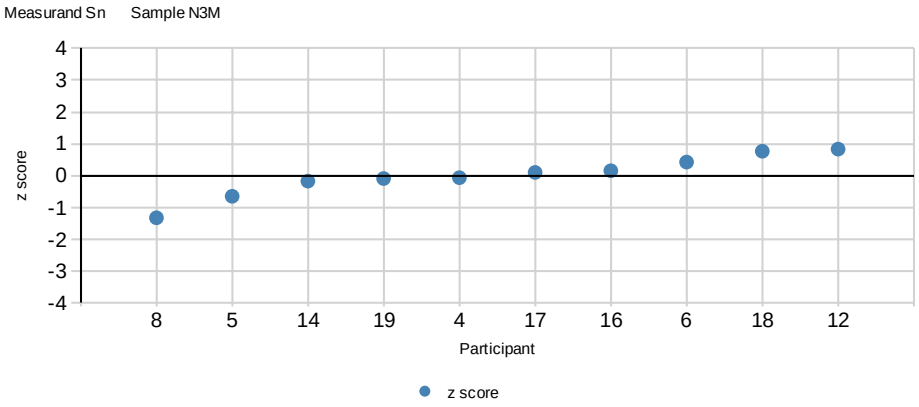


Measurand Se Sample N3M

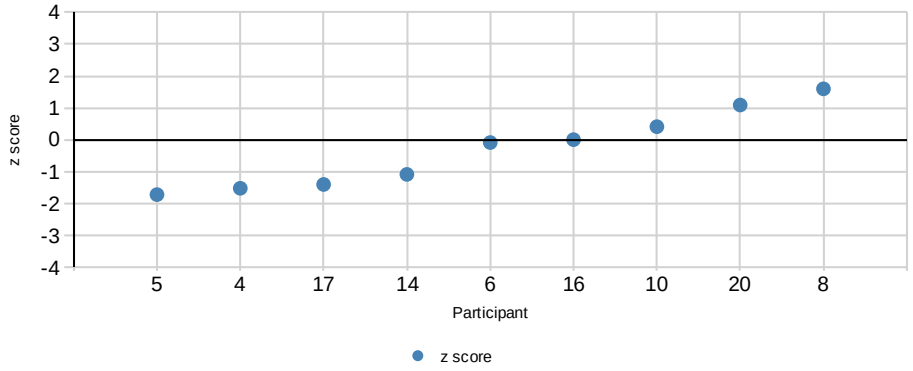



Measurand Sn Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
10 5 8 4 14 16 18 6 17
Participant
z score

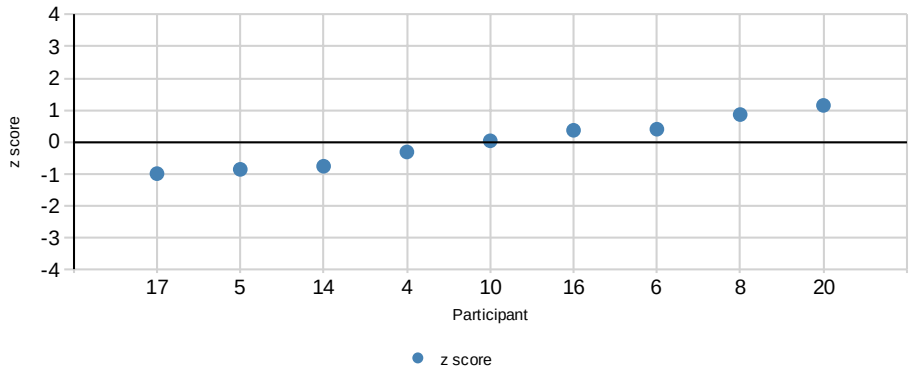

Measurand Sn Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
8 5 14 17 4 16 18 6
Participant
z score


Measurand Sn Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
8 5 14 19 4 17 16 6 18 12
Participant
z score

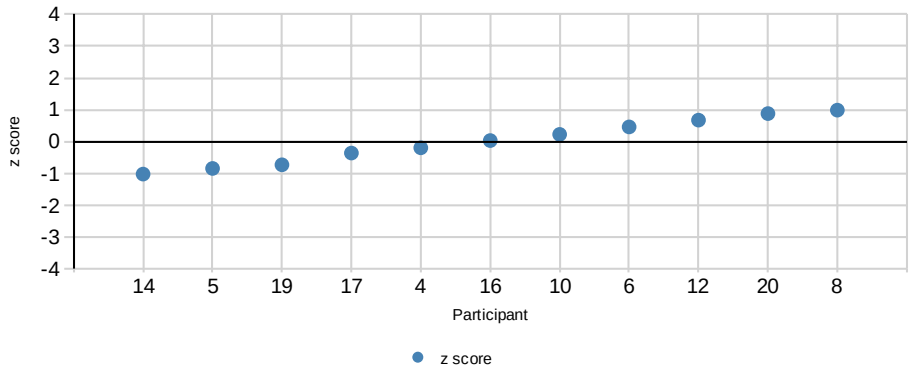
Measurand Sr Sample A1M

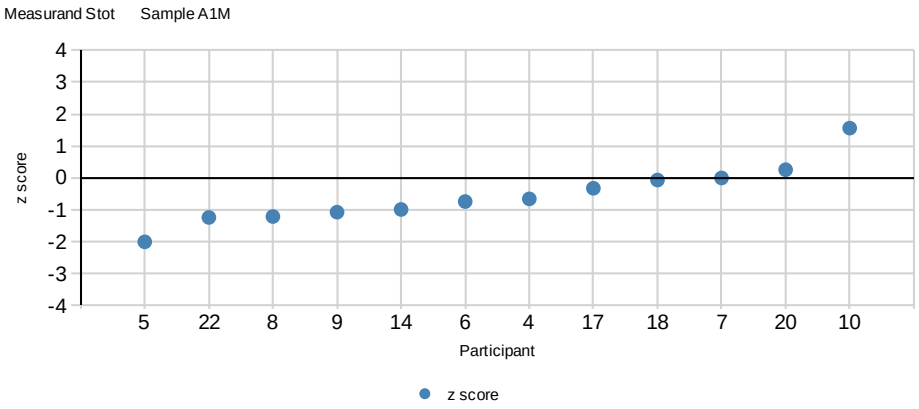


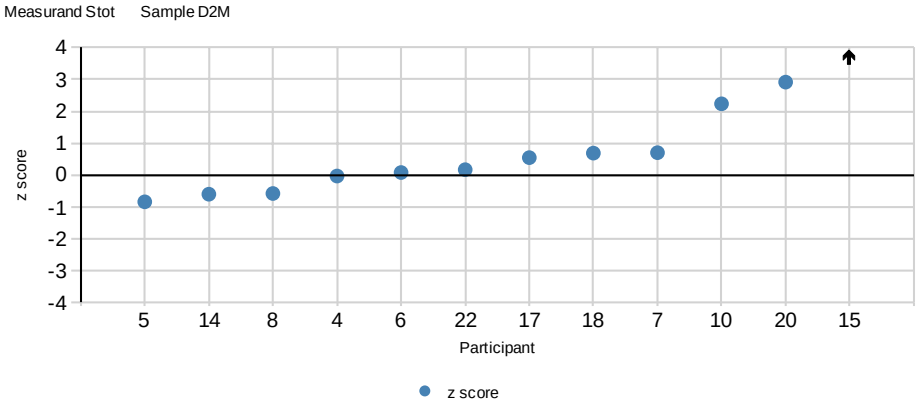
Measurand Sr Sample D2M

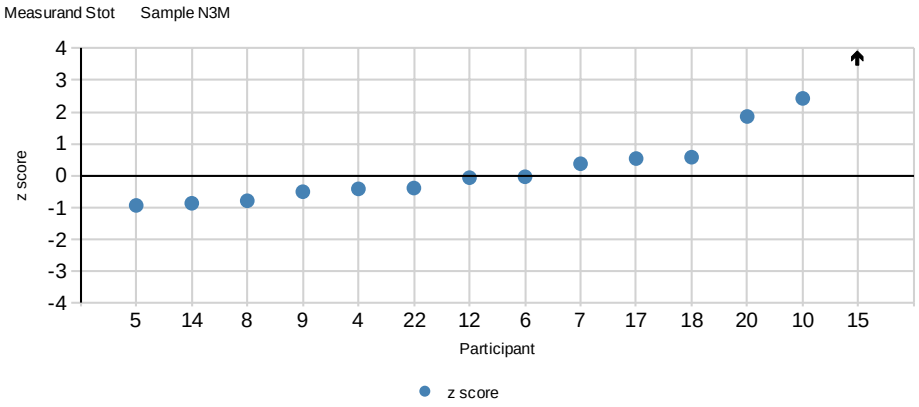


Measurand Sr Sample N3M

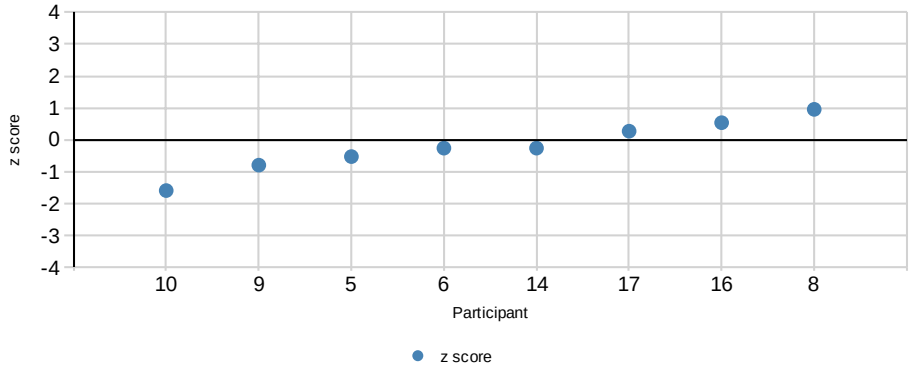



Measurand Stot Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
5 22 8 9 14 6 4 17 18 7 20 10
Participant
z score

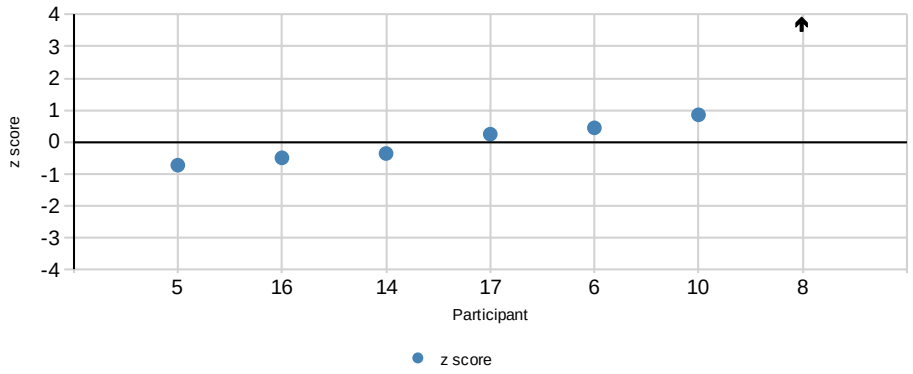

Measurand Stot Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
5 14 8 4 6 22 17 18 7 10 20 15
Participant
z score


Measurand Stot Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
5 14 8 9 4 22 12 6 7 17 18 20 10 15
Participant
z score

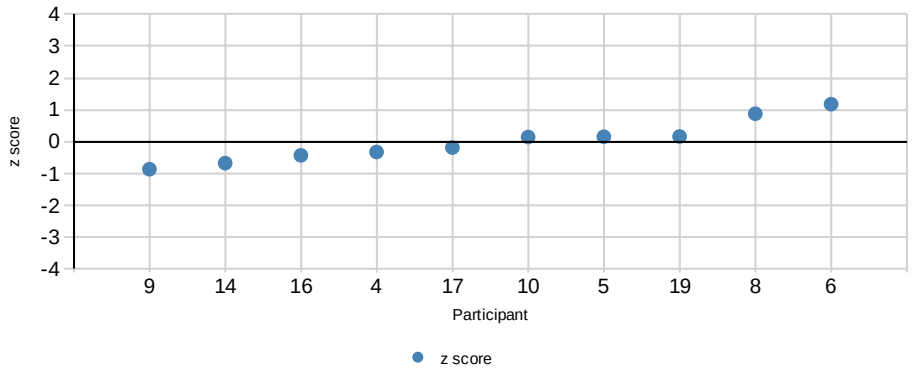
Measurand Ti Sample A1M

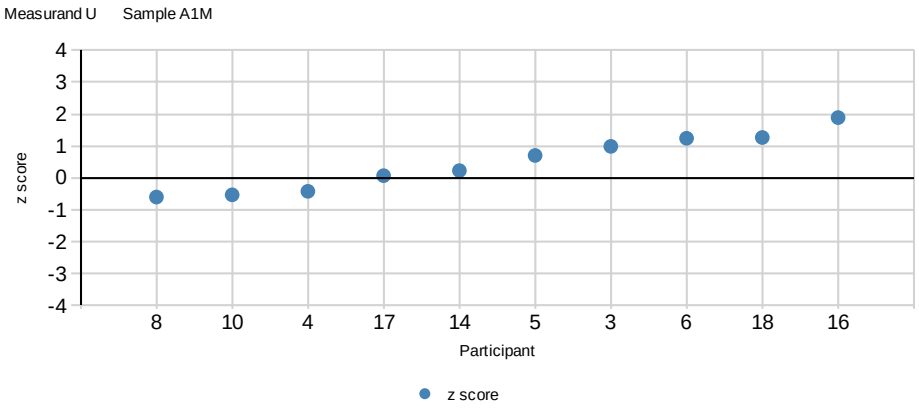


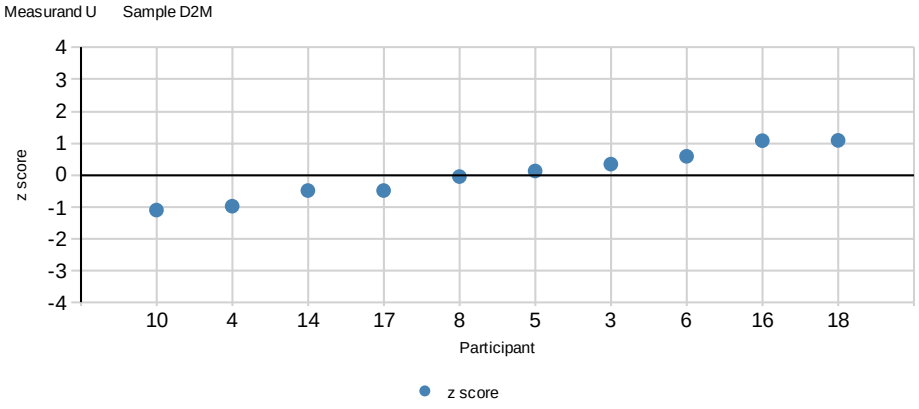
Measurand Ti Sample D2M

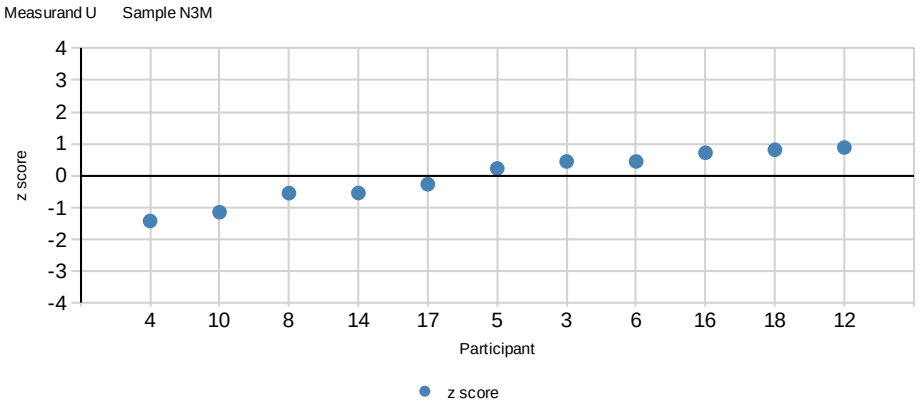


Measurand Ti Sample N3M

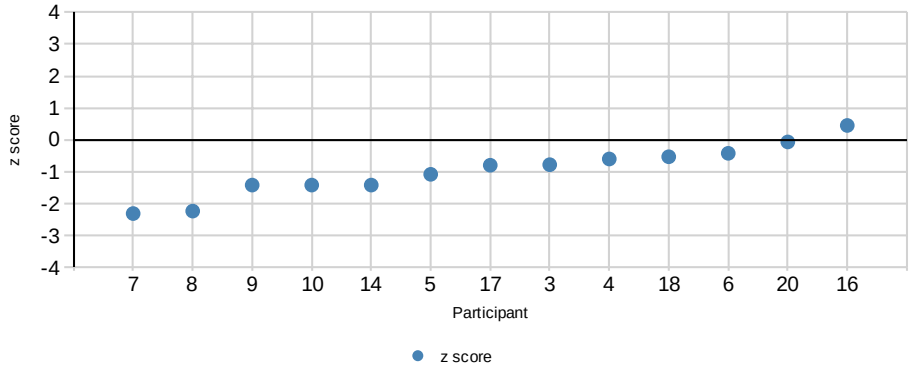



Measurand U Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
8 10 4 17 14 5 3 6 18 16
Participant
z score

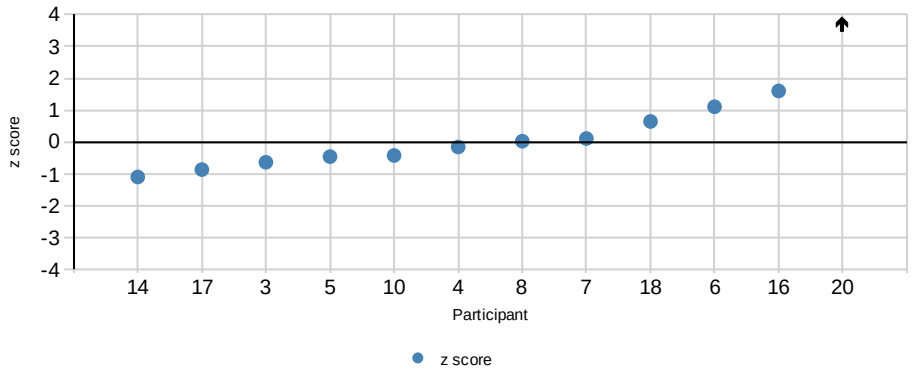

Measurand U Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
10 4 14 17 8 5 3 6 16 18
Participant
z score


Measurand U Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
4 10 8 14 17 5 3 6 16 18 12
Participant
z score

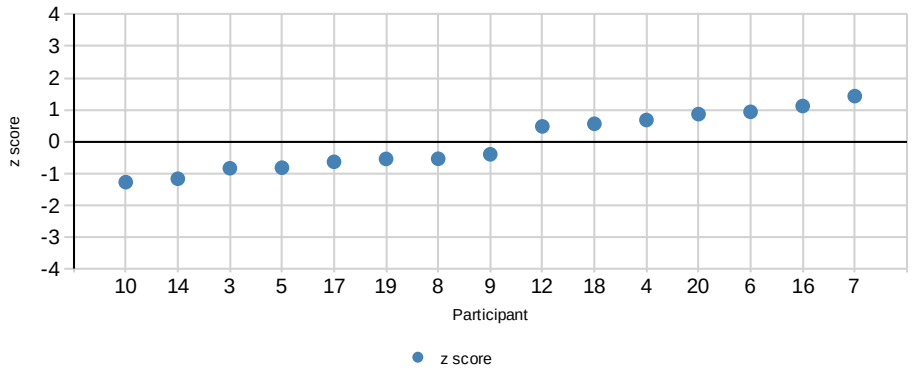
Measurand V Sample A1M

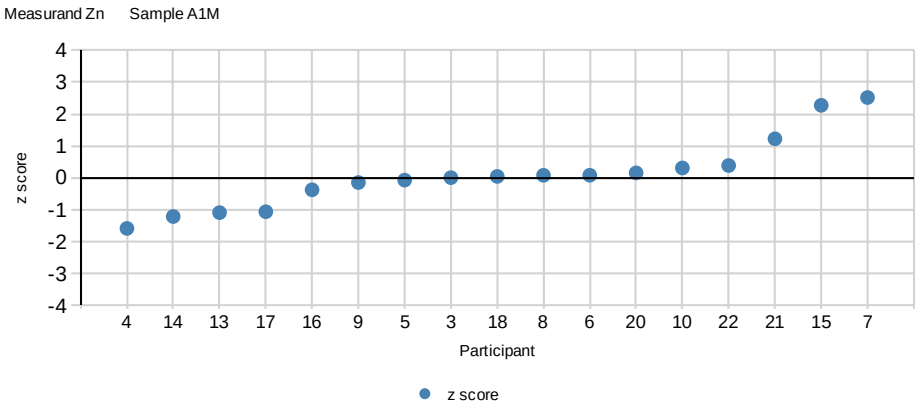


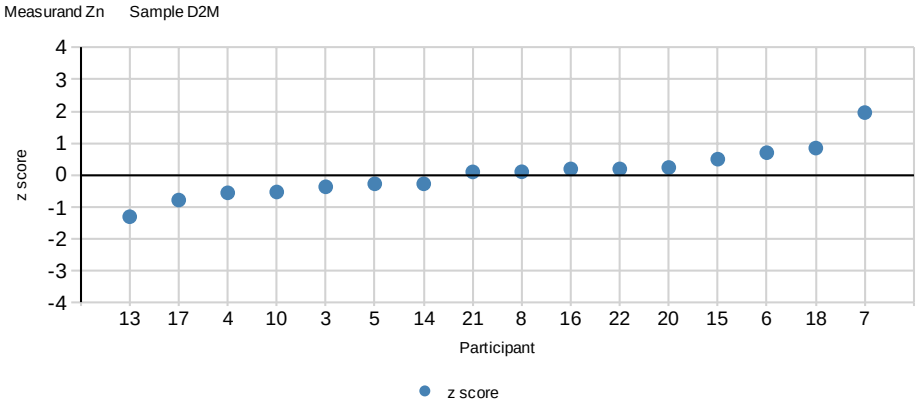
Measurand V Sample D2M

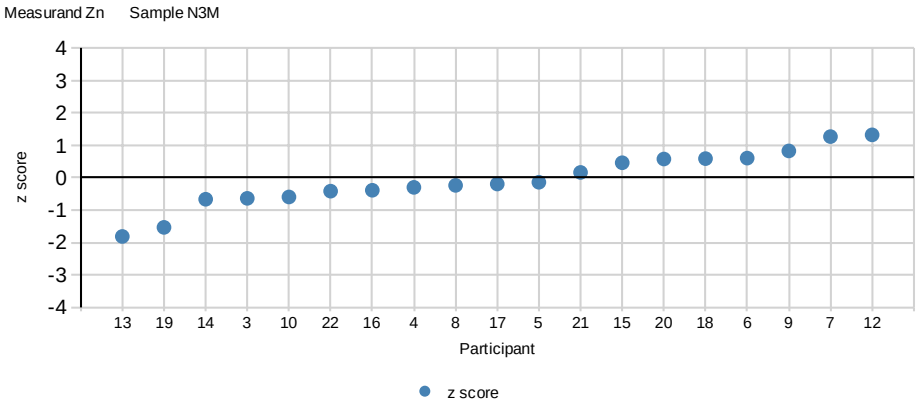


Measurand V Sample N3M




Measurand Zn Sample A1M
z score
4
3
2
1
0
-1
-2
-3
-4
4 14 13 17 16 9 5 3 18 8 6 20 10 22 21 15 7
Participant
z score

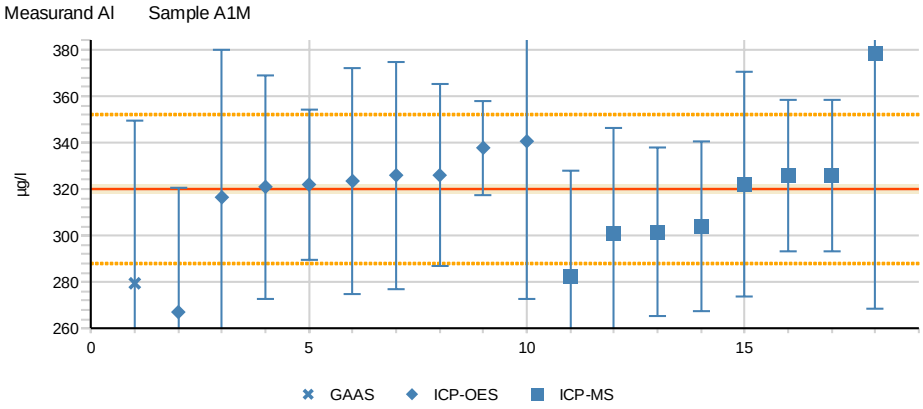

Measurand Zn Sample D2M
z score
4
3
2
1
0
-1
-2
-3
-4
13 17 4 10 3 5 14 21 8 16 22 20 15 6 18 7
Participant
z score

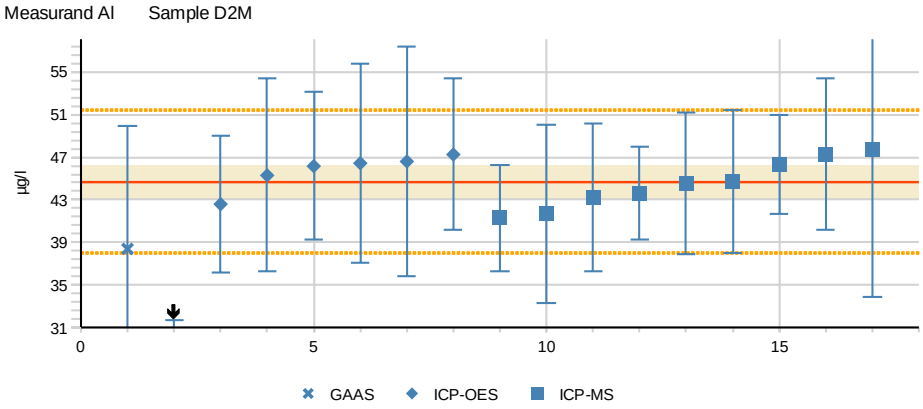

Measurand Zn Sample N3M
z score
4
3
2
1
0
-1
-2
-3
-4
13 19 14 3 10 22 16 4 8 17 5 21 15 20 18 6 9 7 12
Participant
z score

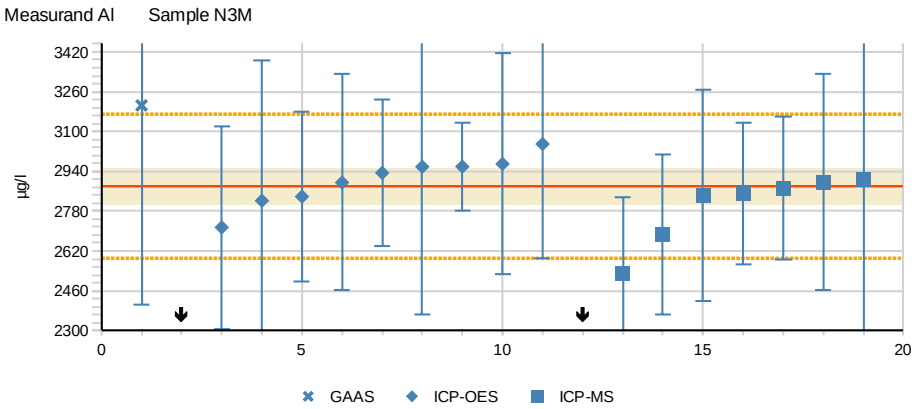
APPENDIX 10: Results grouped according to the methods

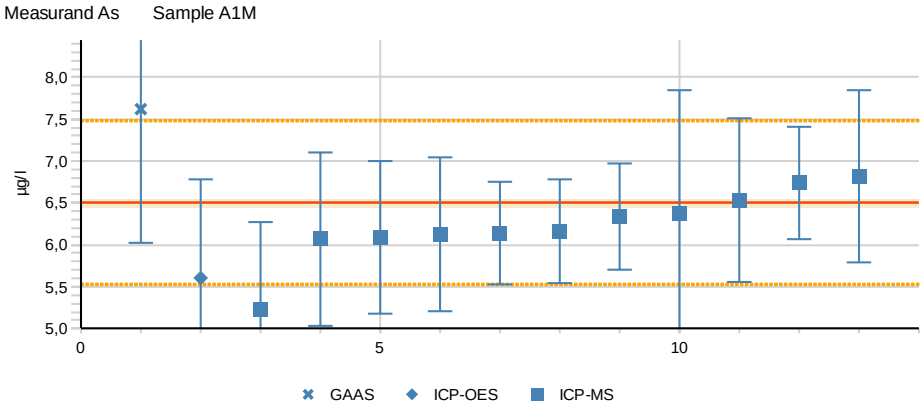
In figures:

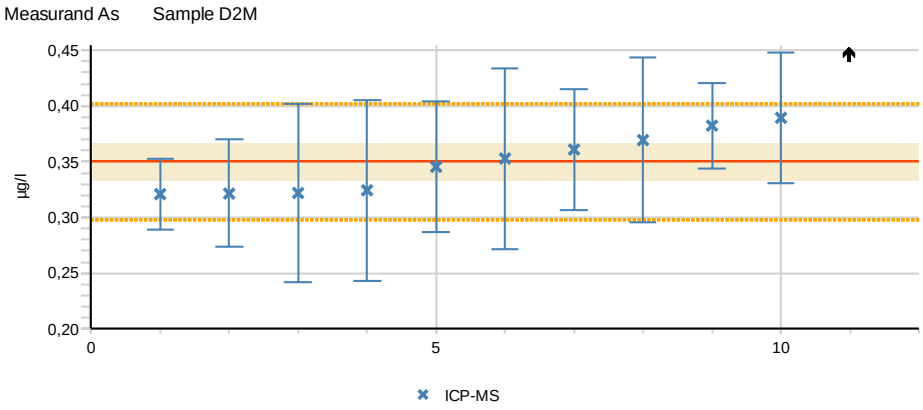
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.

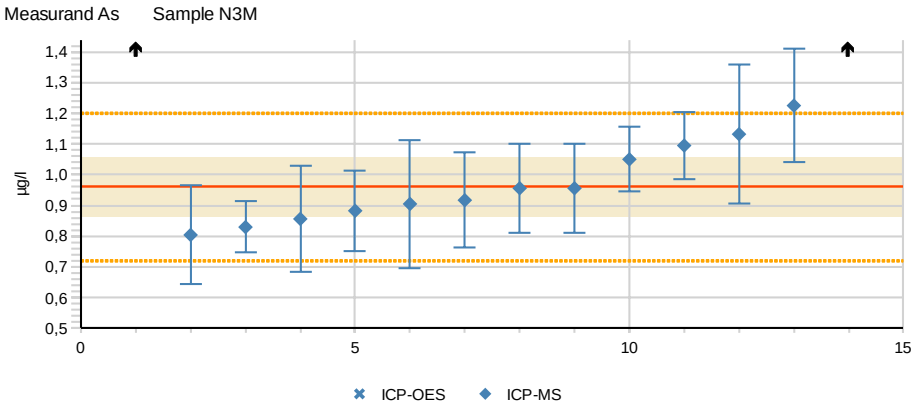




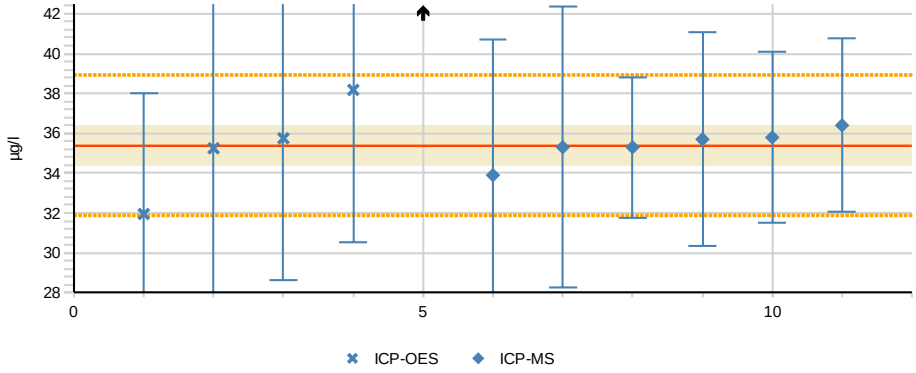



Measurand As
Sample A1M
µg/l
8,0
7,5
7,0
6,5
6,0
5,5
5,0
0
5
10
GAAS
ICP-OES
ICP-MS

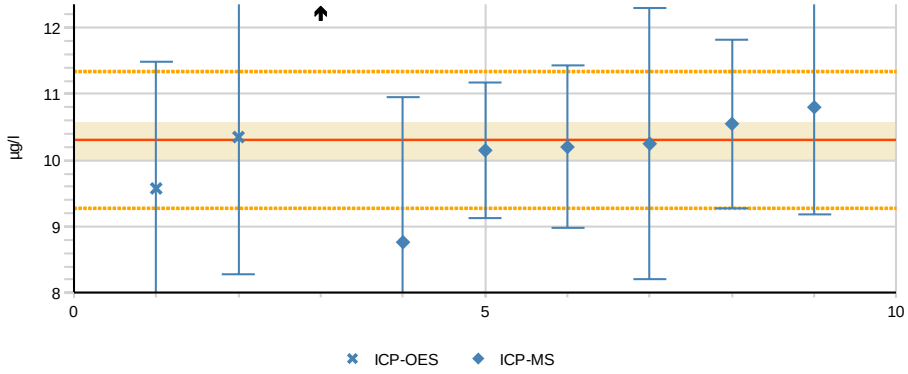

Measurand As
Sample D2M
µg/l
0,45
0,40
0,35
0,30
0,25
0,20
0
5
10
ICP-MS


Measurand As
Sample N3M
µg/l
1,4
1,3
1,2
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0
5
10
15
ICP-OES
ICP-MS

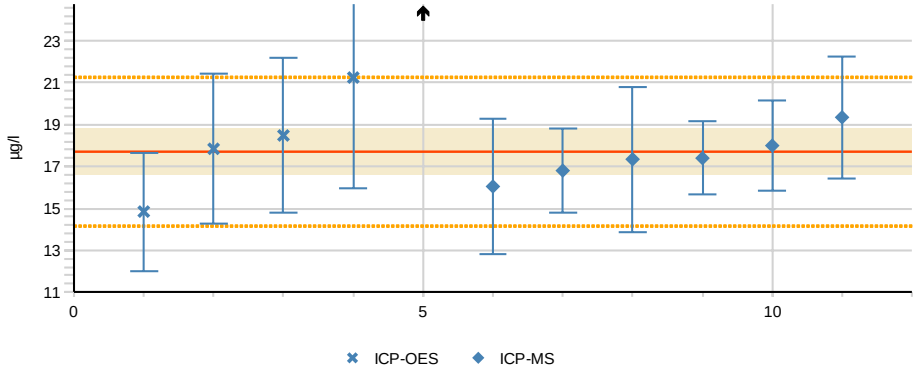
Measurand B Sample A1M

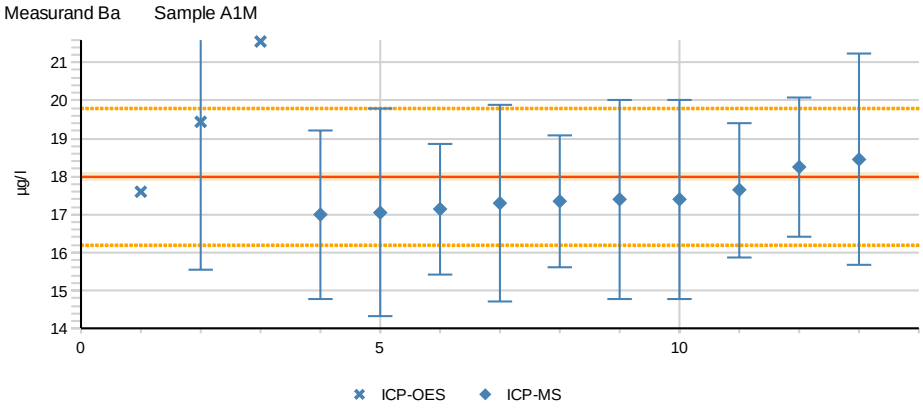


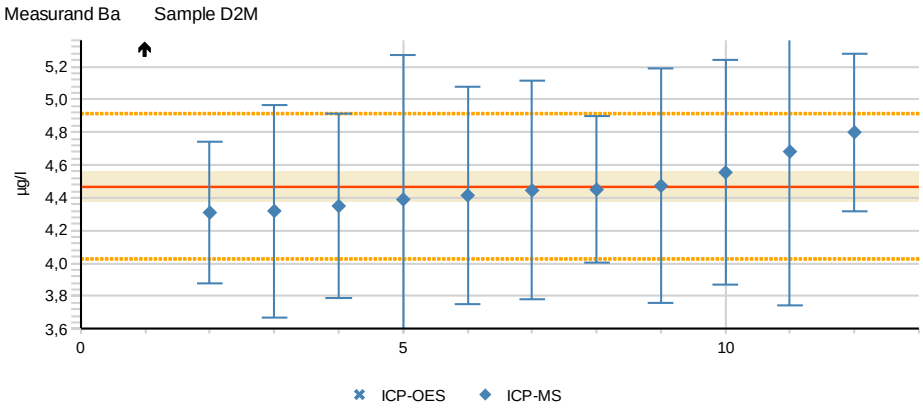
Measurand B Sample D2M

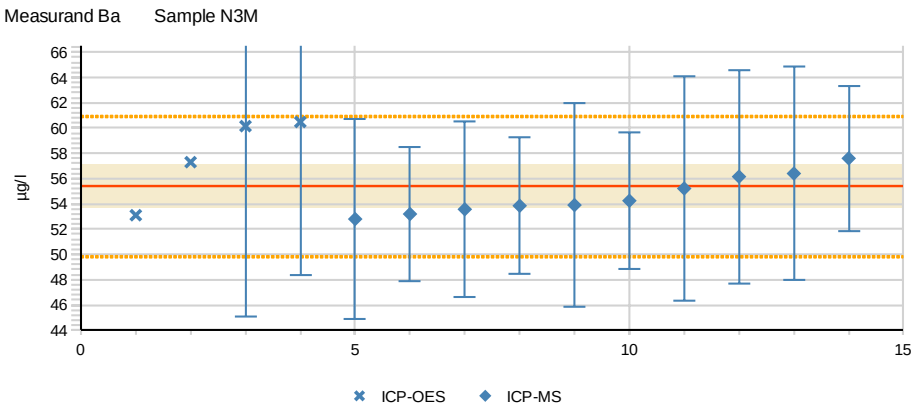


Measurand B Sample N3M

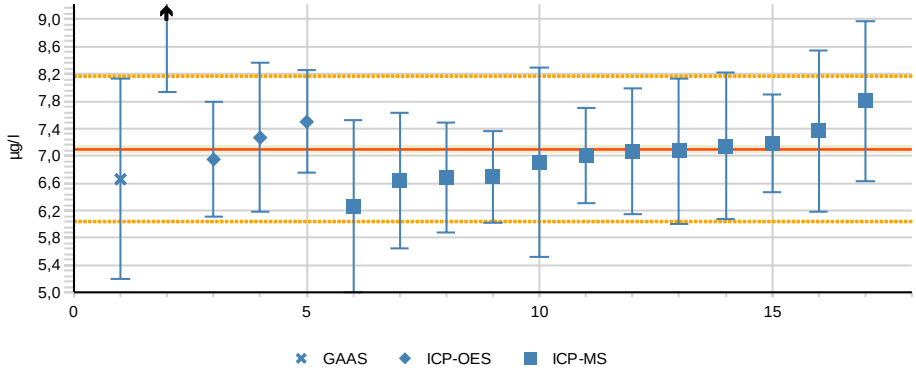



Measurand Ba
Sample A1M
µg/l
21
20
19
18
17
16
15
14
0
5
10
ICP-OES
ICP-MS

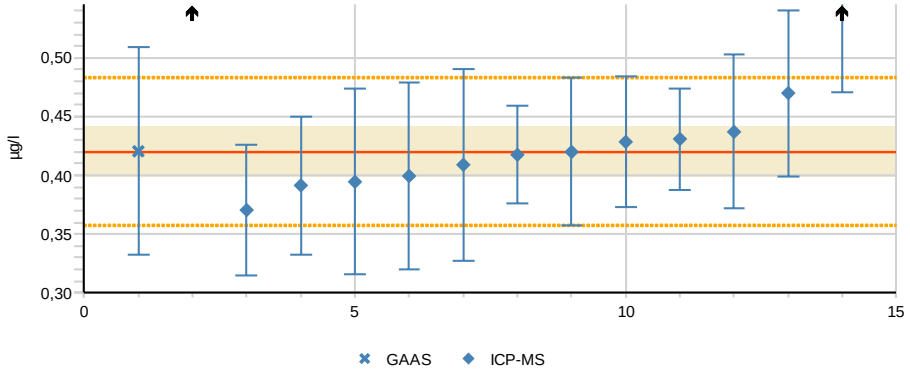

Measurand Ba
Sample D2M
µg/l
5,2
5,0
4,8
4,6
4,4
4,2
4,0
3,8
3,6
0
5
10
ICP-OES
ICP-MS


Measurand Ba
Sample N3M
µg/l
66
64
62
60
58
56
54
52
50
48
46
44
0
5
10
15
ICP-OES
ICP-MS

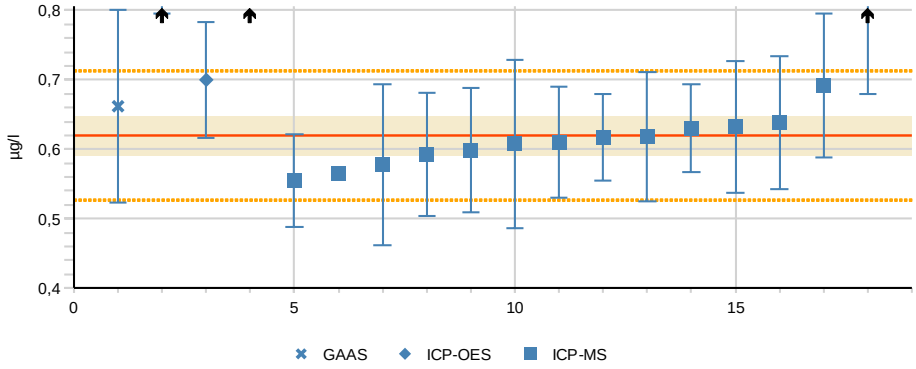
Measurand Cd Sample A1M



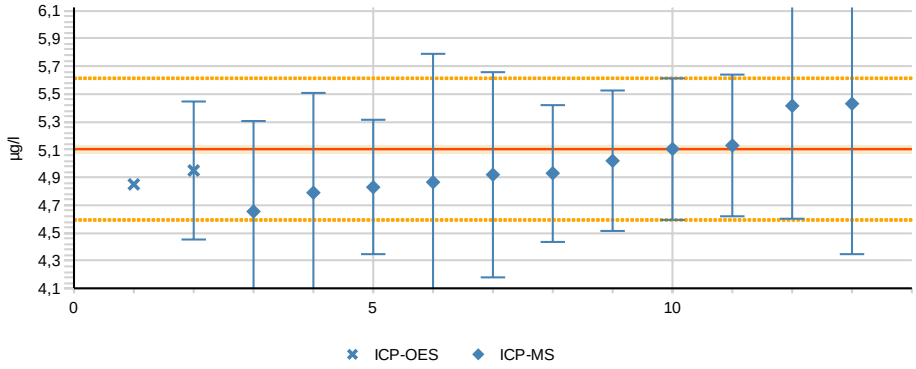
Measurand Cd Sample D2M



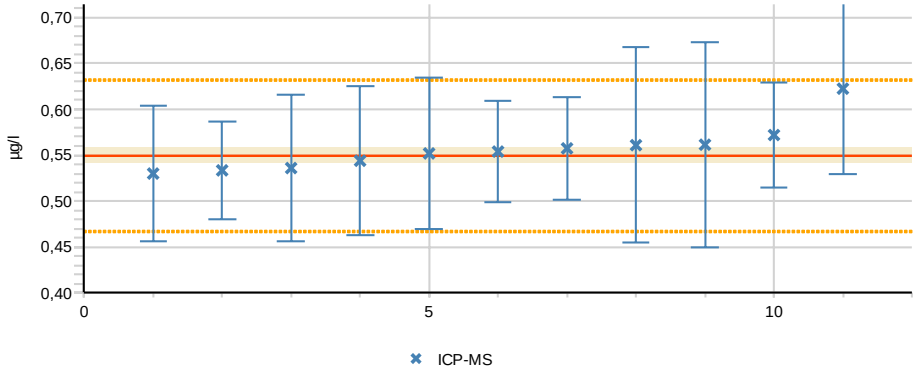
Measurand Cd Sample N3M



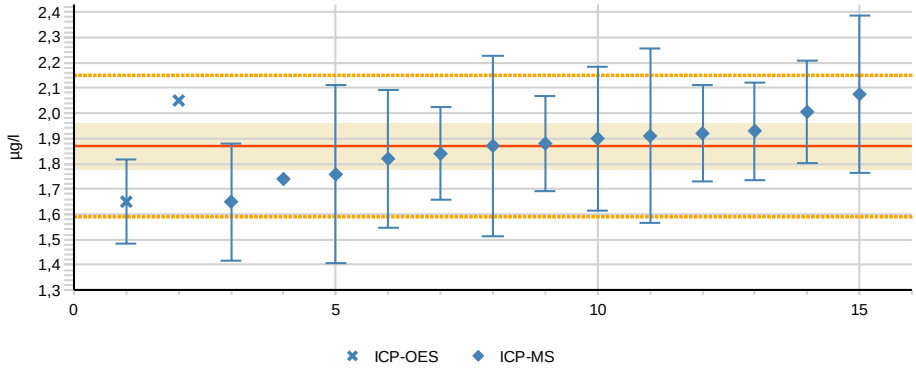
Measurand Co Sample A1M



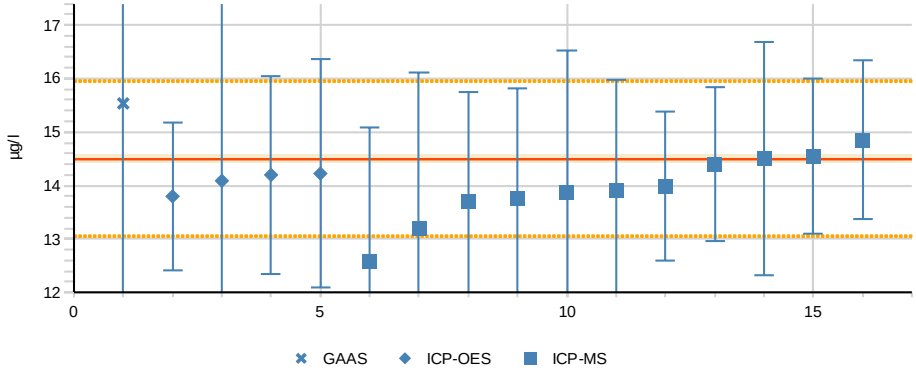
Measurand Co Sample D2M



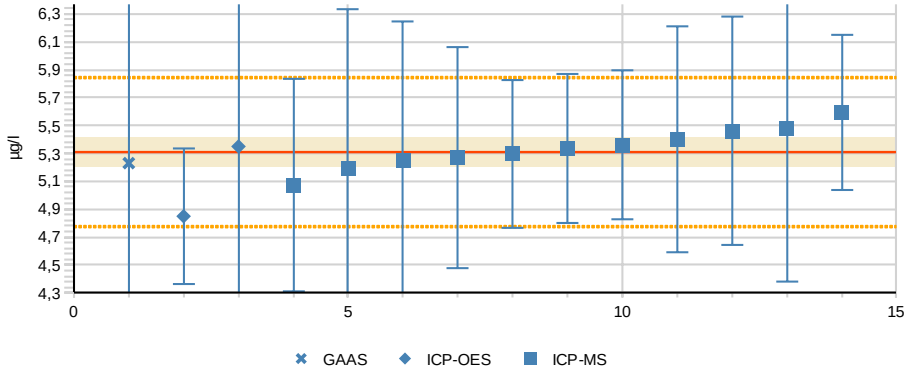
Measurand Co Sample N3M



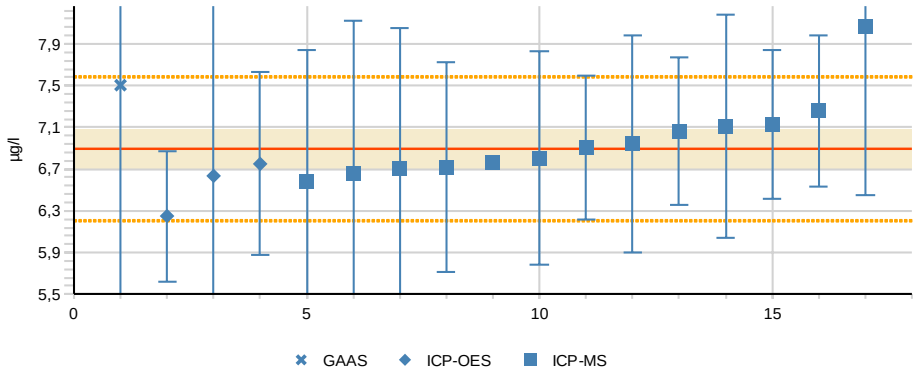
Measurand Cr Sample A1M

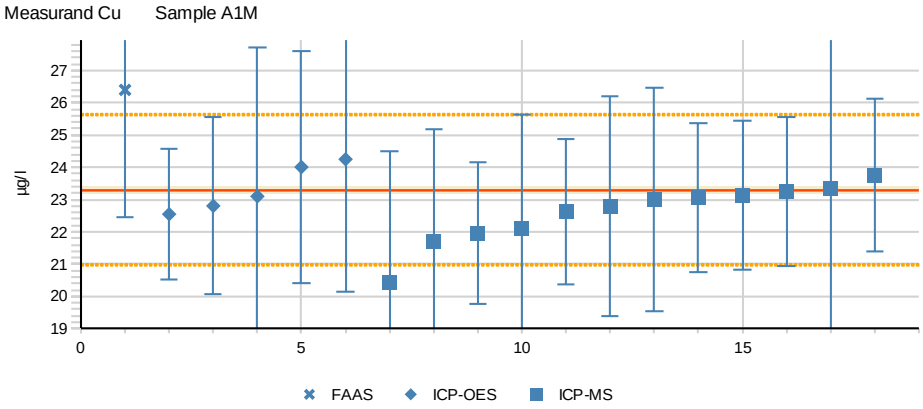


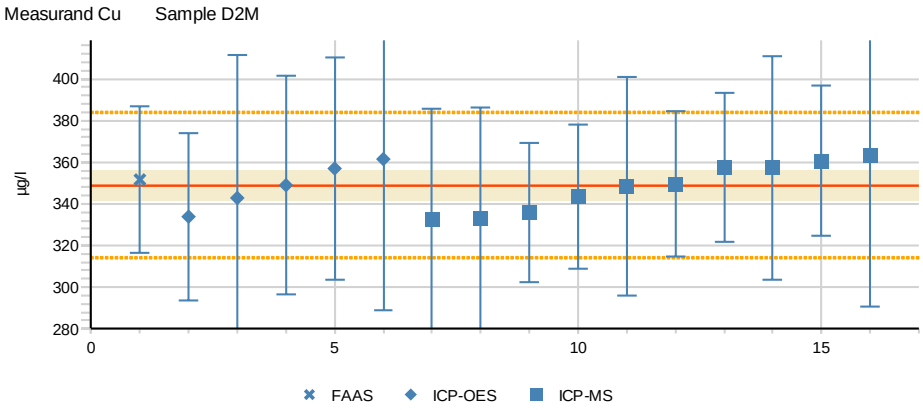
Measurand Cr Sample D2M

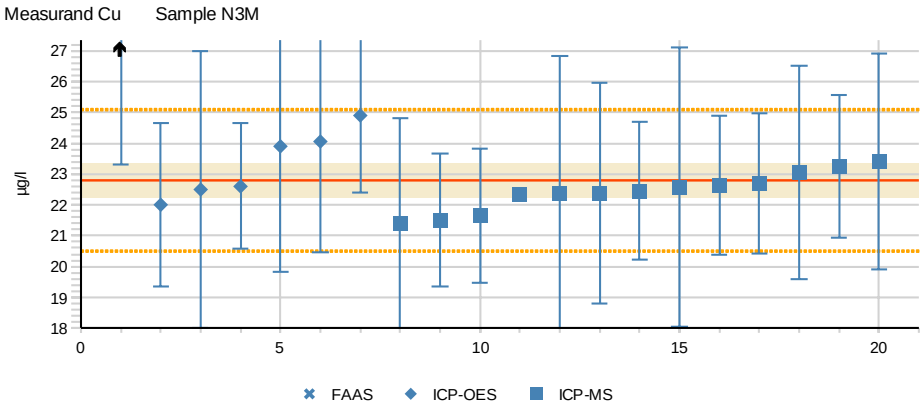


Measurand Cr Sample N3M

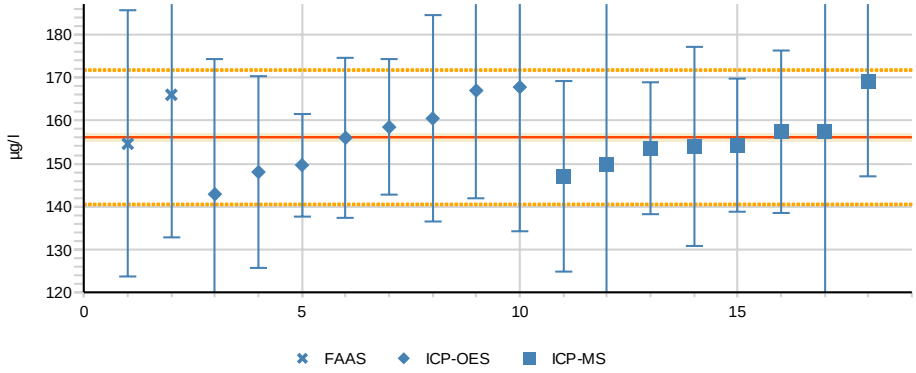



Measurand Cu
Sample A1M
µg/l
27
26
25
24
23
22
21
20
19
0
5
10
15
FAAS
ICP-OES
ICP-MS

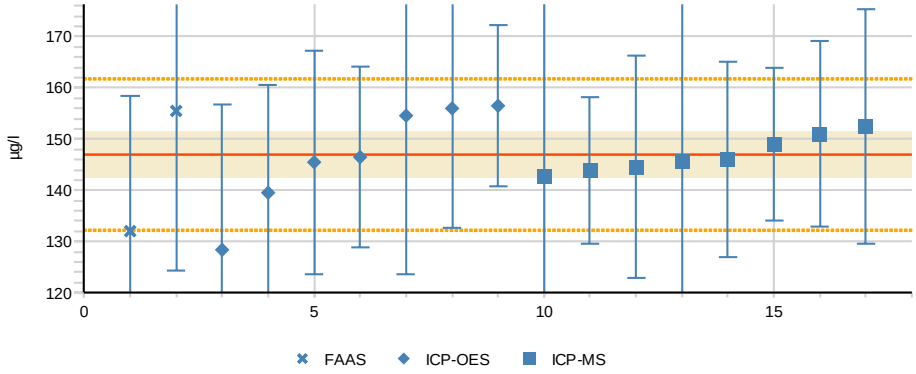

Measurand Cu
Sample D2M
µg/l
400
380
360
340
320
300
280
0
5
10
15
FAAS
ICP-OES
ICP-MS


Measurand Cu
Sample N3M
µg/l
27
26
25
24
23
22
21
20
19
18
0
5
10
15
20
FAAS
ICP-OES
ICP-MS

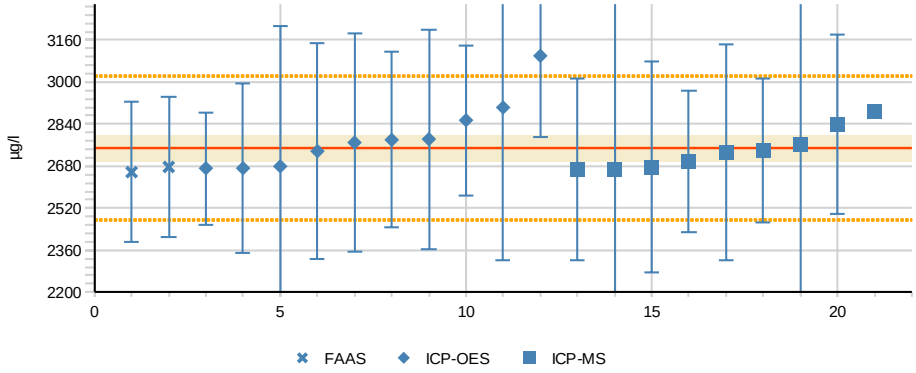
Measurand Fe Sample A1M

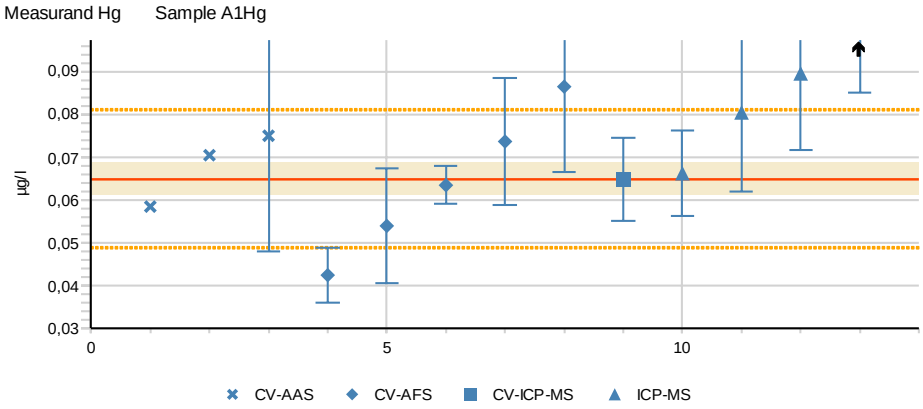


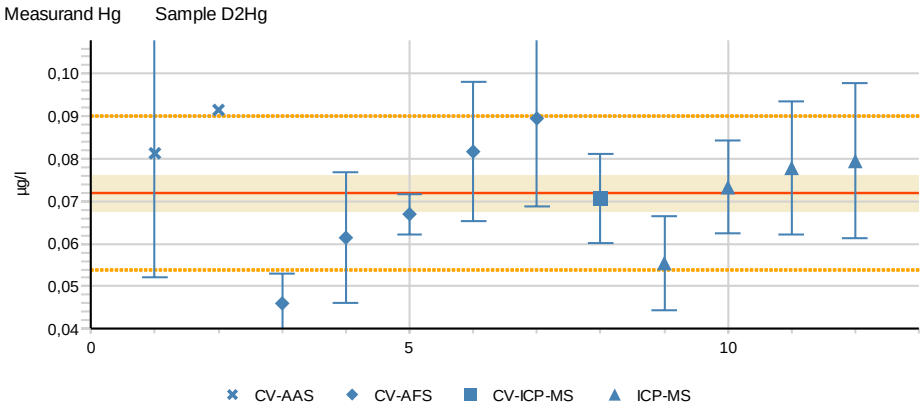
Measurand Fe Sample D2M

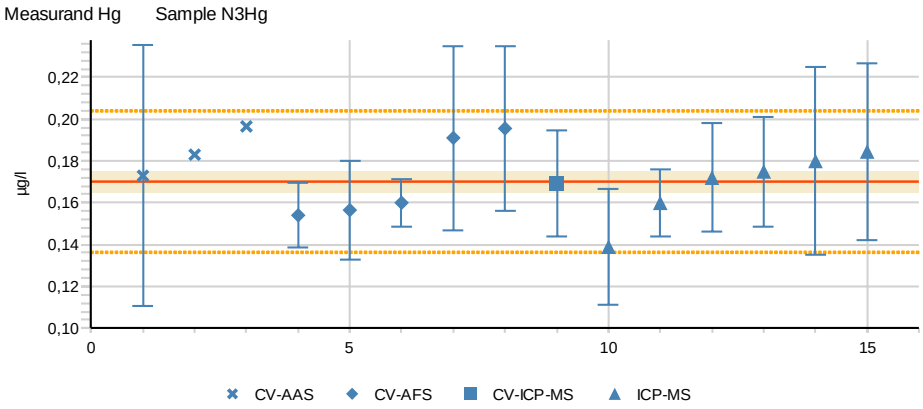


Measurand Fe Sample N3M

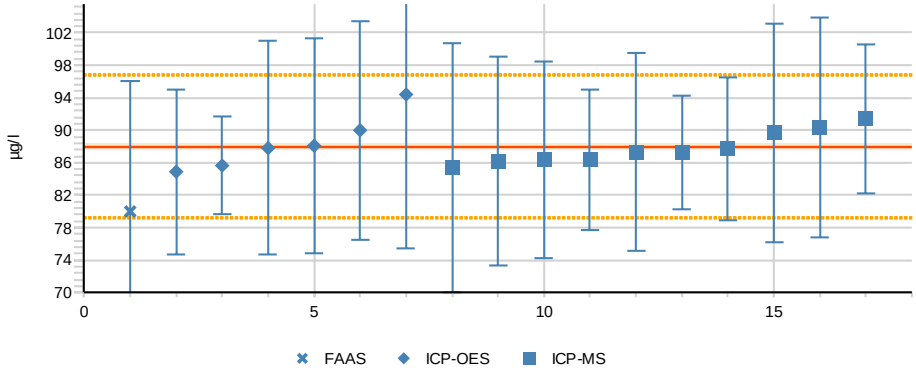



Measurand Hg
Sample A1Hg
µg/l
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS

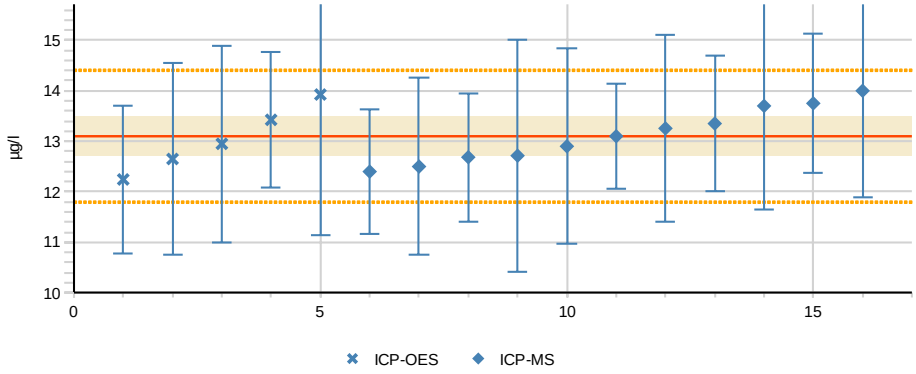

Measurand Hg
Sample D2Hg
µg/l
0,10
0,09
0,08
0,07
0,06
0,05
0,04
0
5
10
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS


Measurand Hg
Sample N3Hg
µg/l
0,22
0,20
0,18
0,16
0,14
0,12
0,10
0
5
10
15
CV-AAS
CV-AFS
CV-ICP-MS
ICP-MS

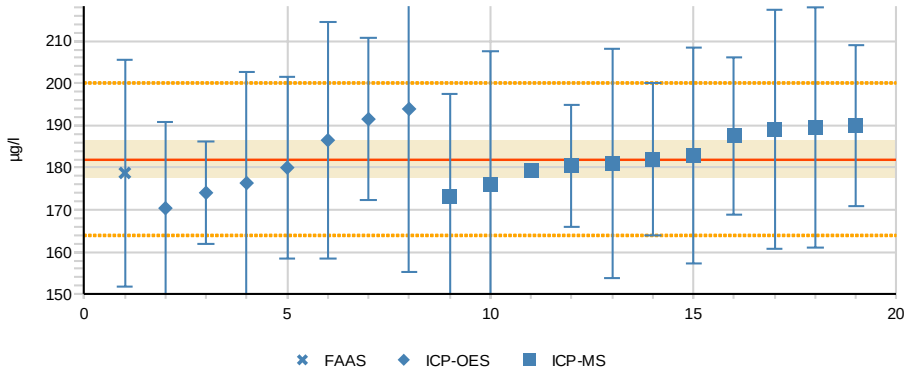
Measurand Mn Sample A1M

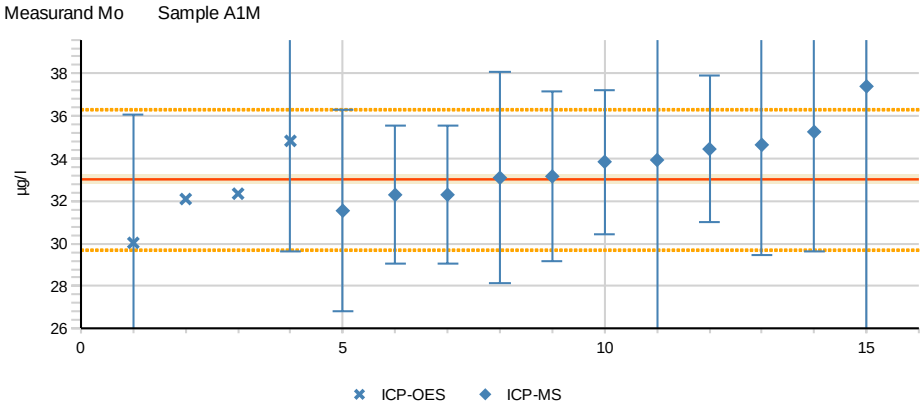


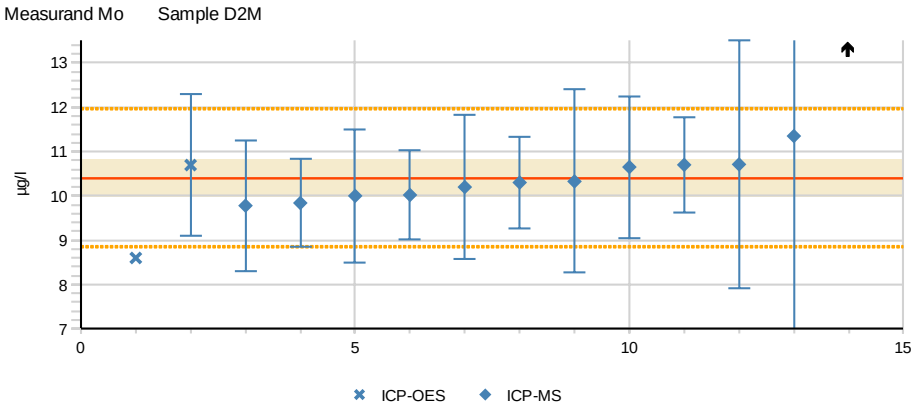
Measurand Mn Sample D2M

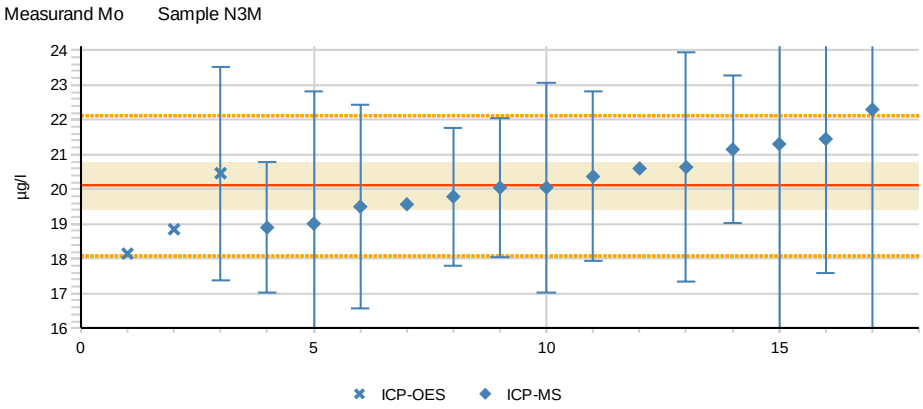


Measurand Mn Sample N3M

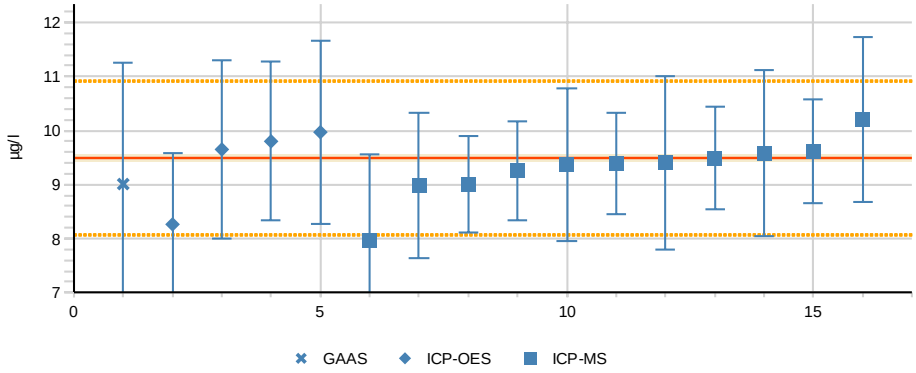



Measurand Mo
Sample A1M
µg/l
38
36
34
32
30
28
26
0
5
10
15
ICP-OES
ICP-MS

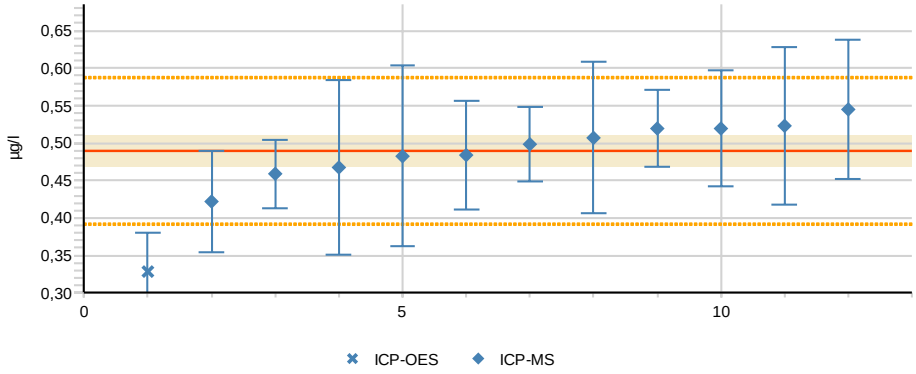

Measurand Mo
Sample D2M
µg/l
13
12
11
10
9
8
7
0
5
10
15
ICP-OES
ICP-MS


Measurand Mo
Sample N3M
µg/l
24
23
22
21
20
19
18
17
16
0
5
10
15
ICP-OES
ICP-MS

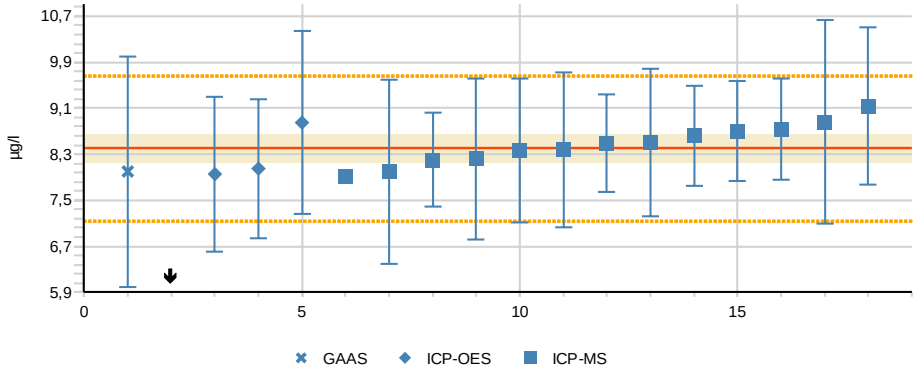
Measurand Ni Sample A1M



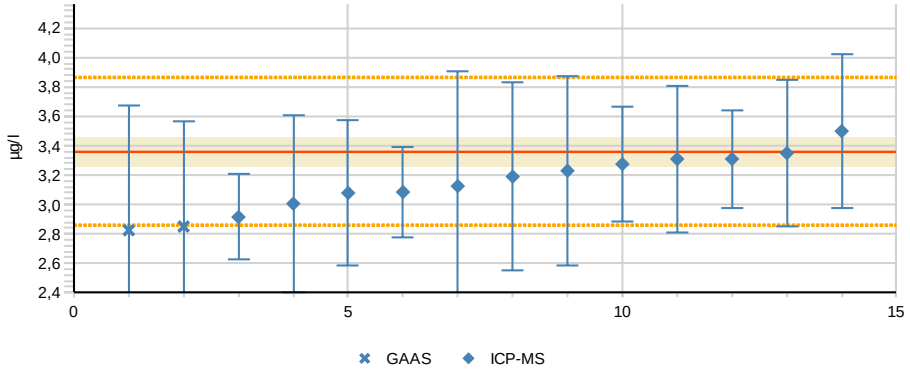
Measurand Ni Sample D2M



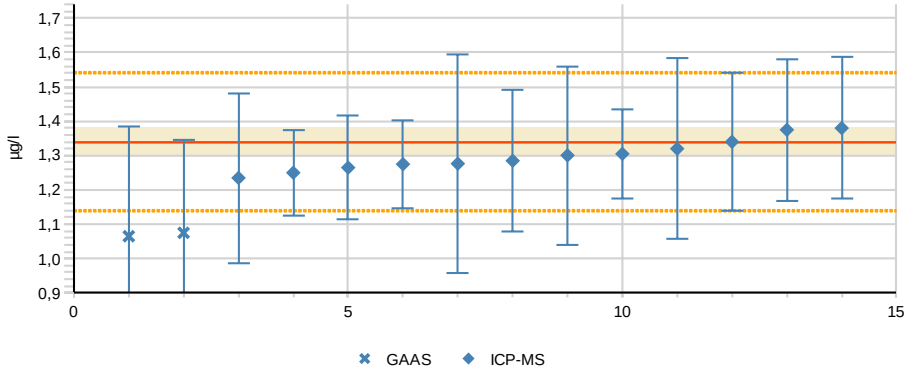
Measurand Ni Sample N3M



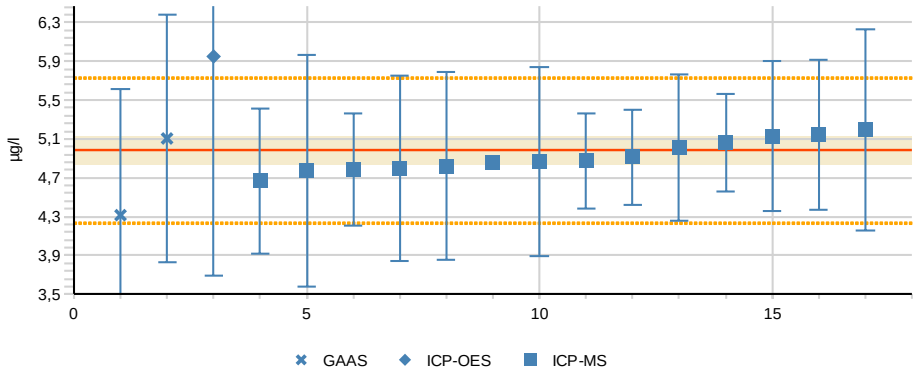
Measurand Pb Sample A1M



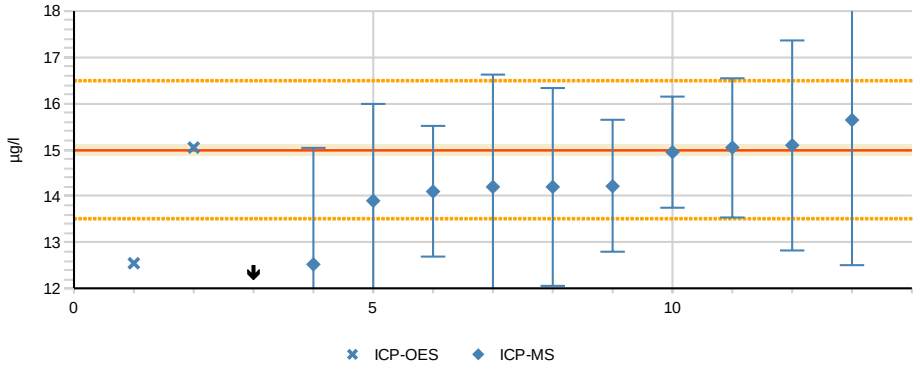
Measurand Pb Sample D2M



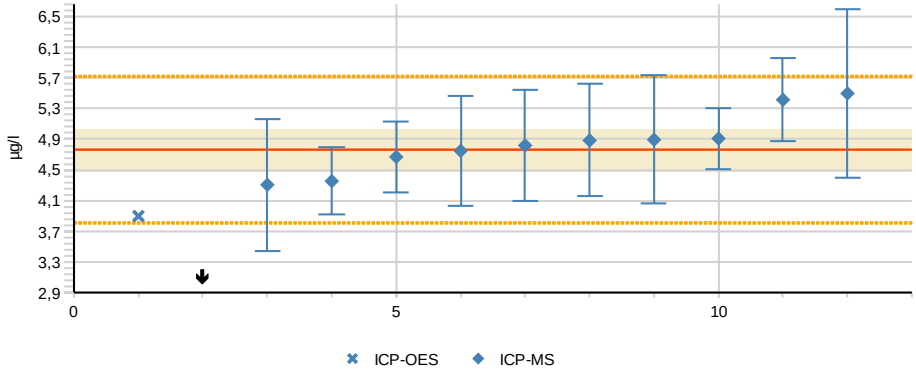
Measurand Pb Sample N3M



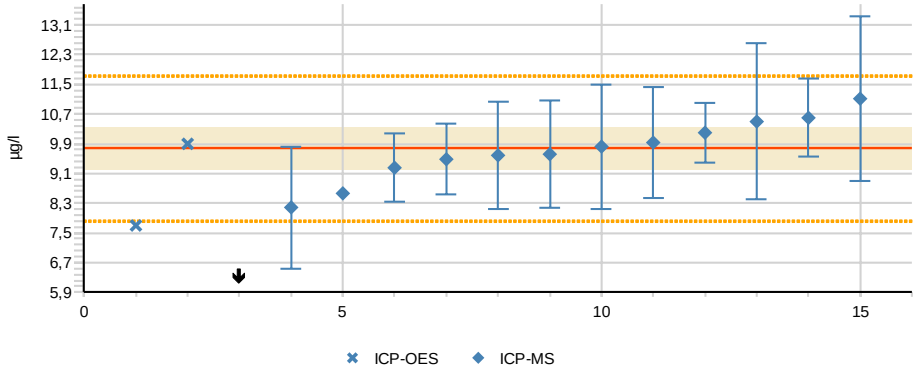
Measurand Sb Sample A1M



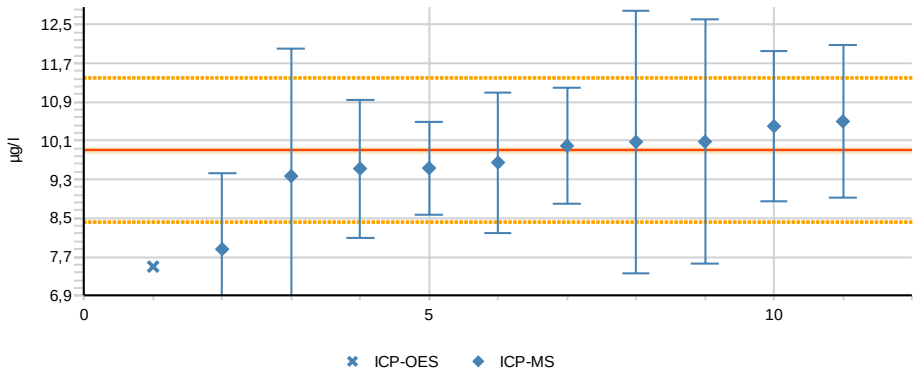
Measurand Sb Sample D2M



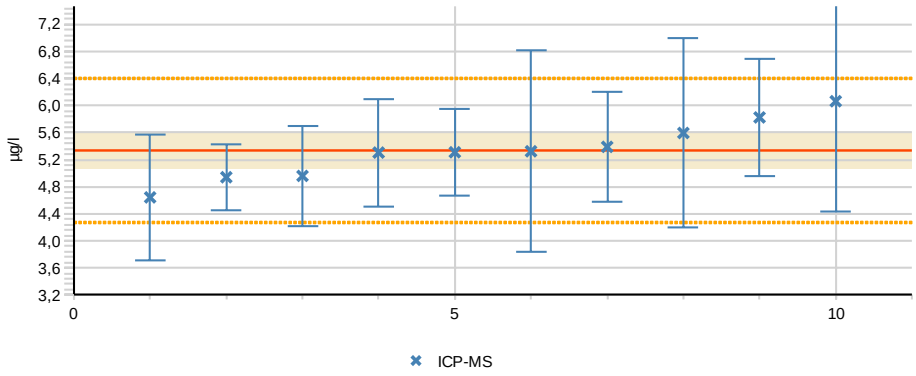
Measurand Sb Sample N3M



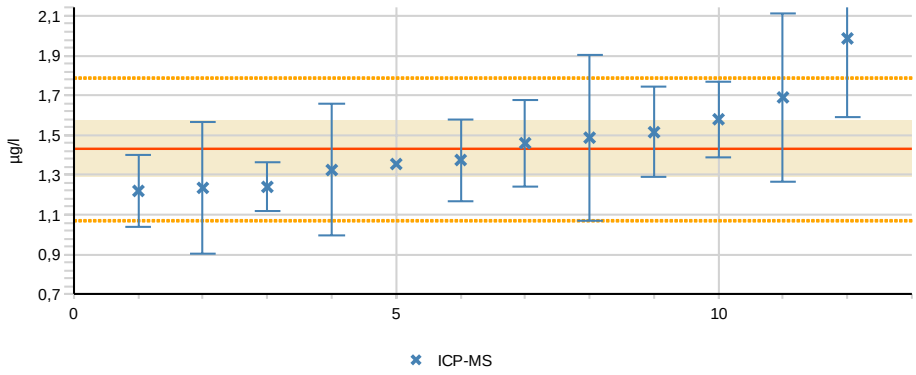
Measurand Se Sample A1M



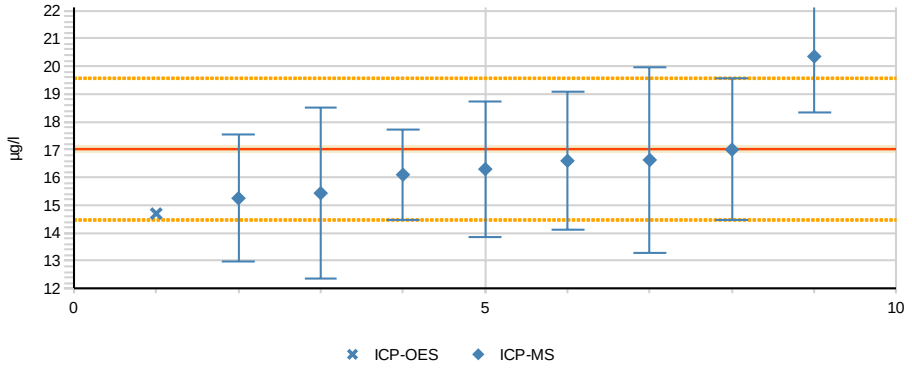
Measurand Se Sample D2M



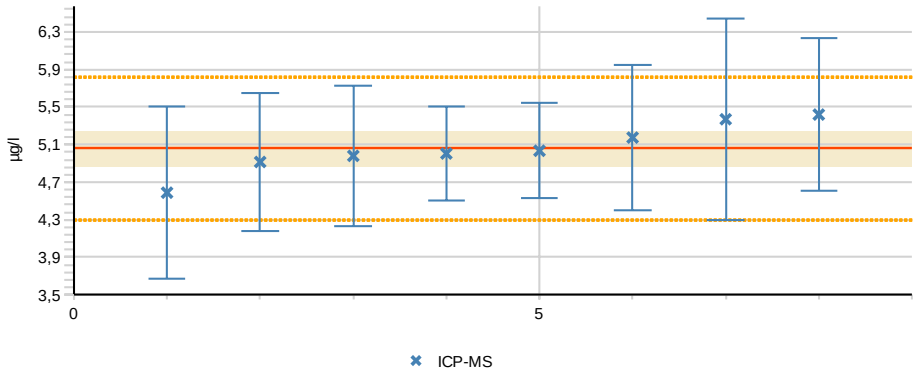
Measurand Se Sample N3M



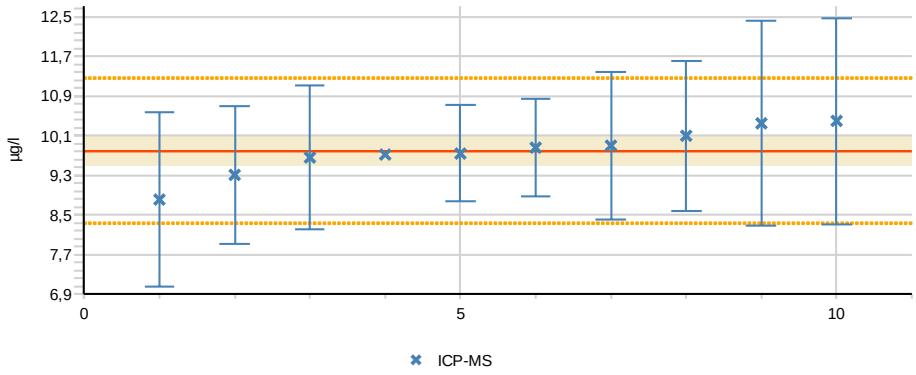
Measurand Sn Sample A1M

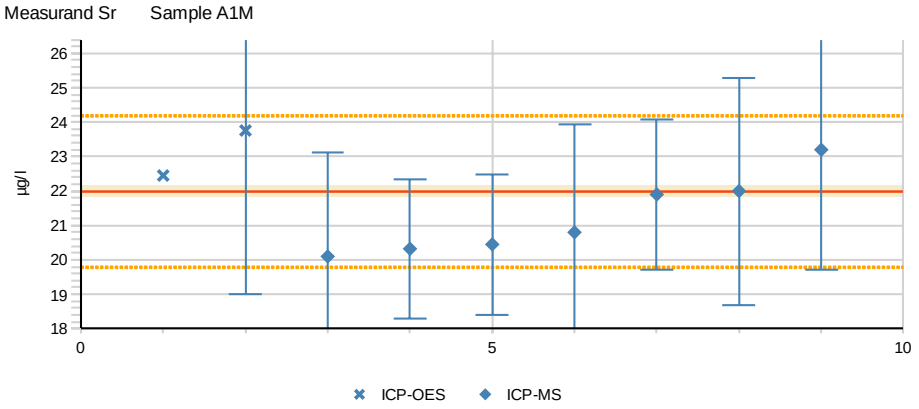


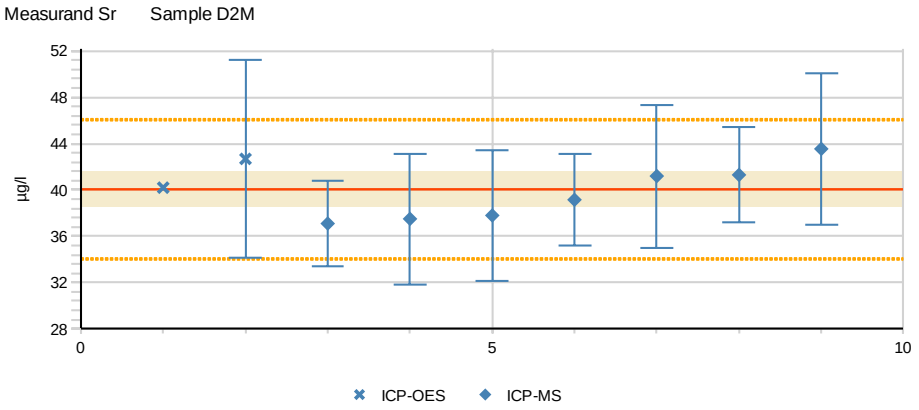
Measurand Sn Sample D2M

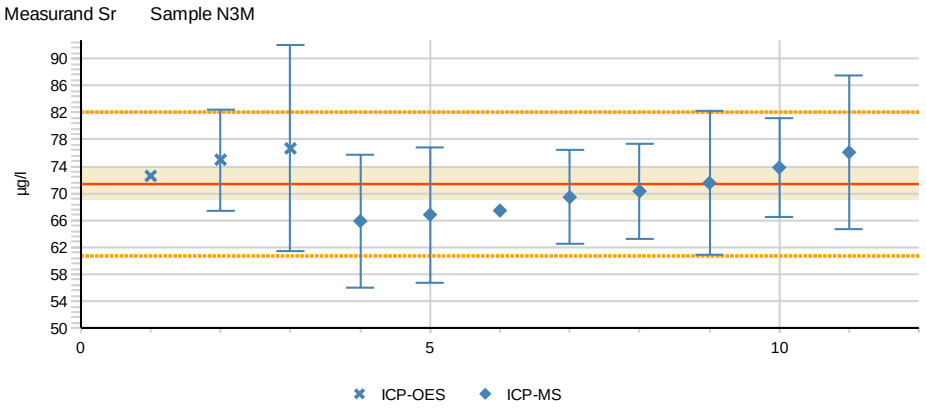


Measurand Sn Sample N3M

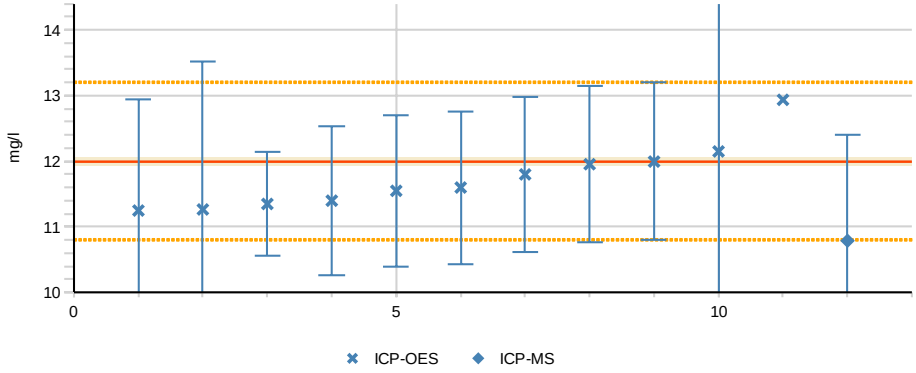



Measurand Sr
Sample A1M
µg/l
26
25
24
23
22
21
20
19
18
0
5
10
ICP-OES
ICP-MS

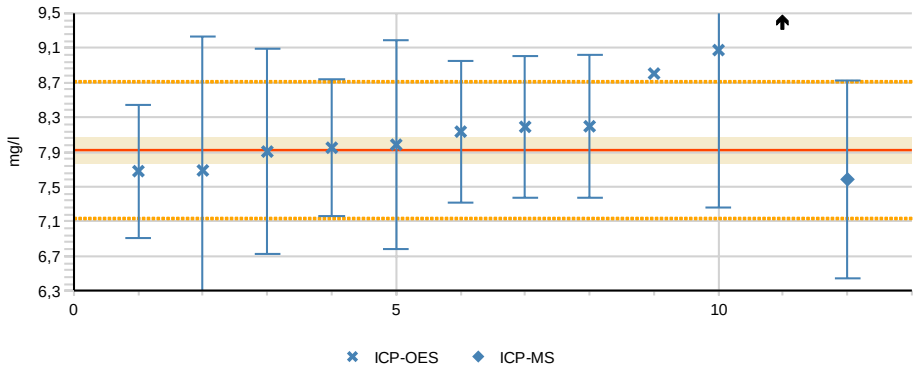

Measurand Sr
Sample D2M
µg/l
52
48
44
40
36
32
28
0
5
10
ICP-OES
ICP-MS


Measurand Sr
Sample N3M
µg/l
90
86
82
78
74
70
66
62
58
54
50
0
5
10
ICP-OES
ICP-MS

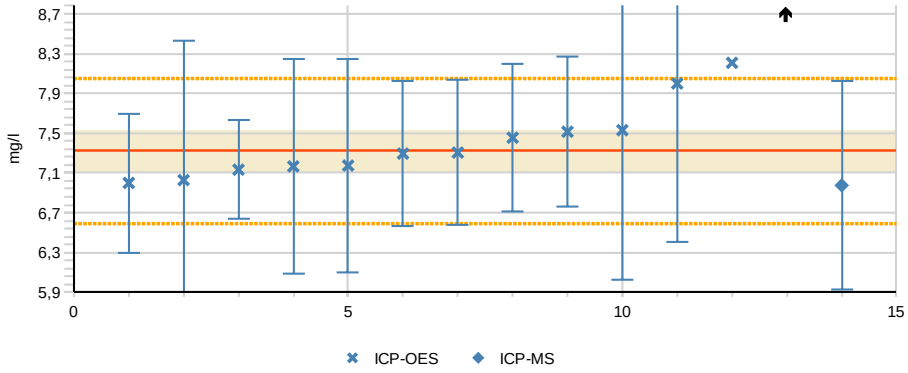
Measurand Stot Sample A1M



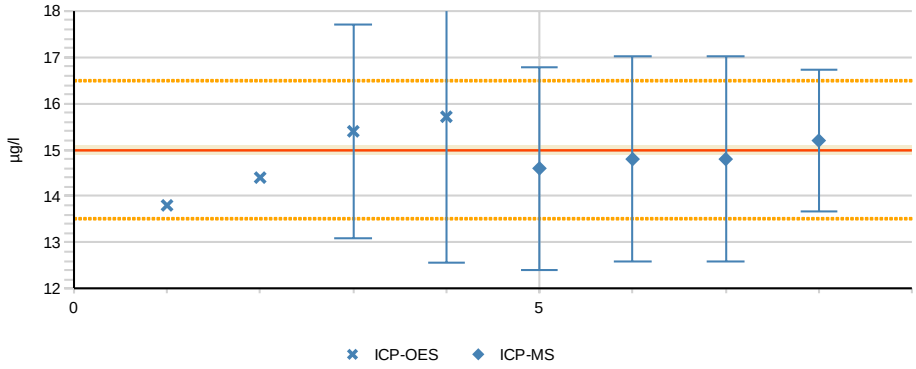
Measurand Stot Sample D2M



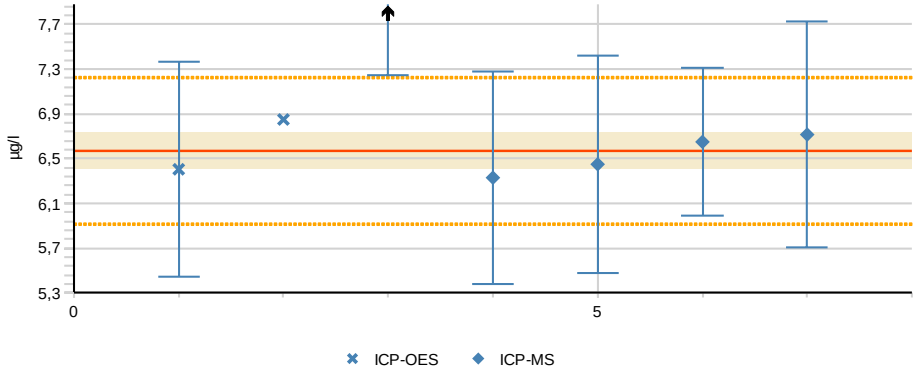
Measurand Stot Sample N3M



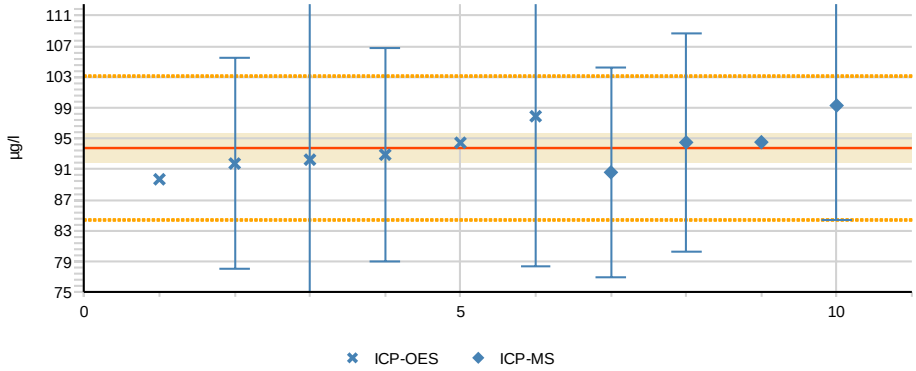
Measurand Ti Sample A1M



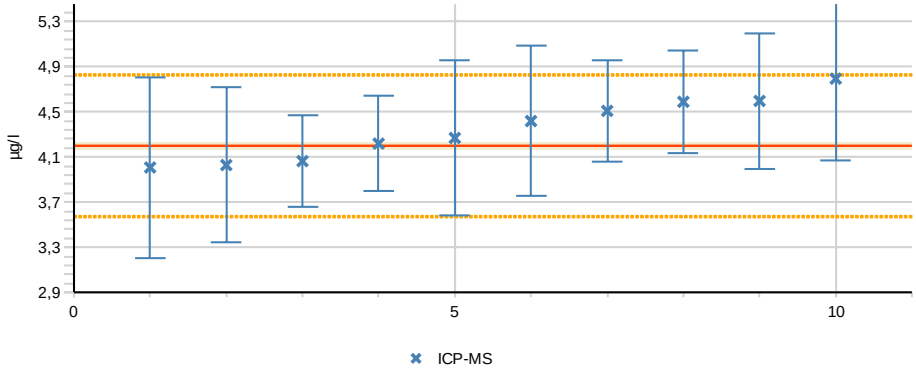
Measurand Ti Sample D2M



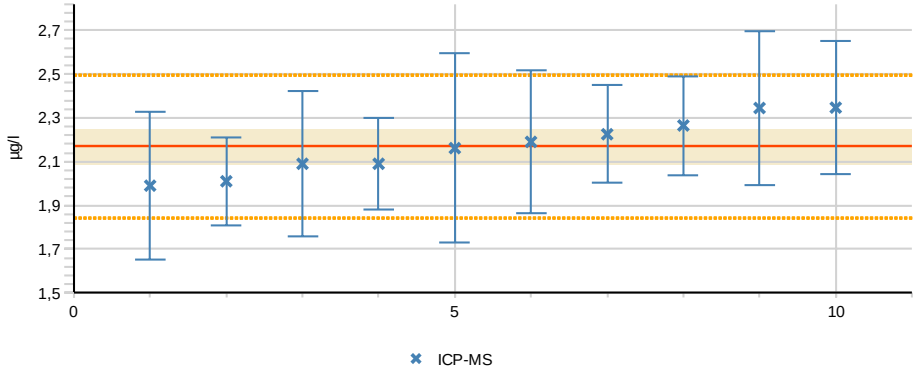
Measurand Ti Sample N3M



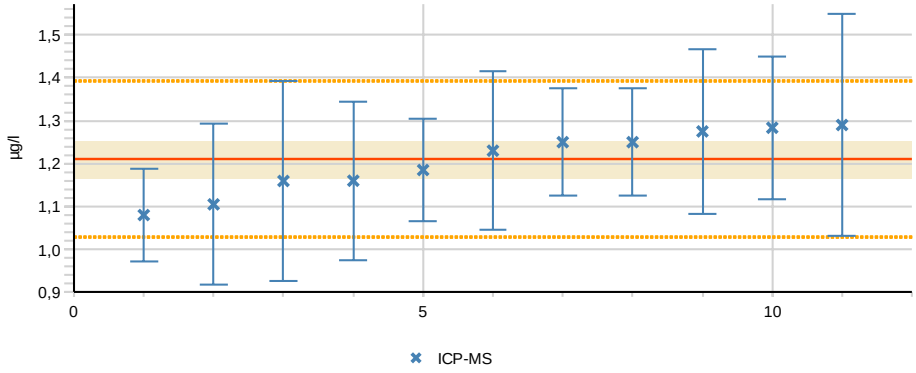
Measurand U Sample A1M



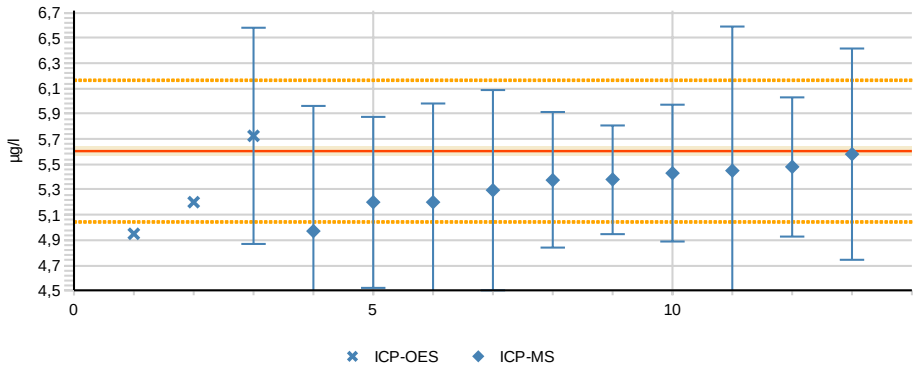
Measurand U Sample D2M



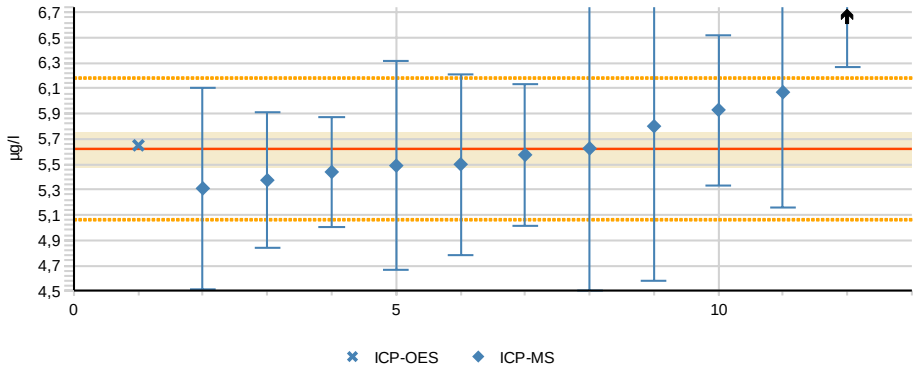
Measurand U Sample N3M



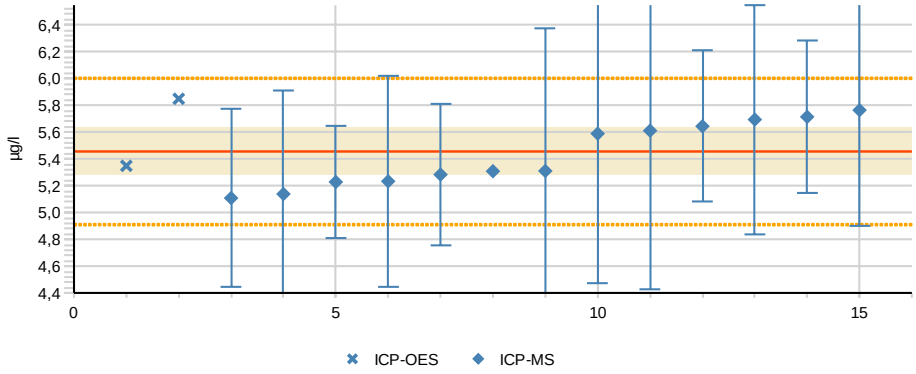
Measurand V Sample A1M



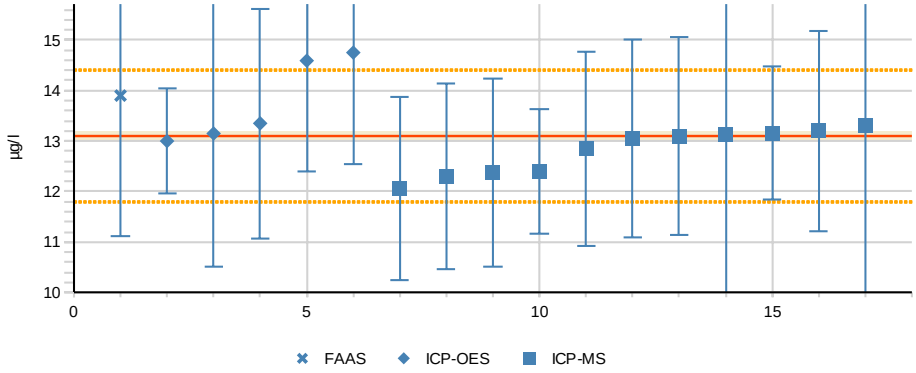
Measurand V Sample D2M



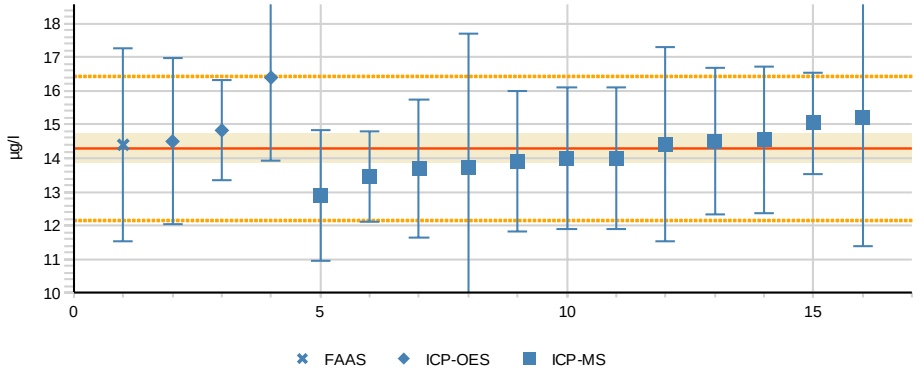
Measurand V Sample N3M



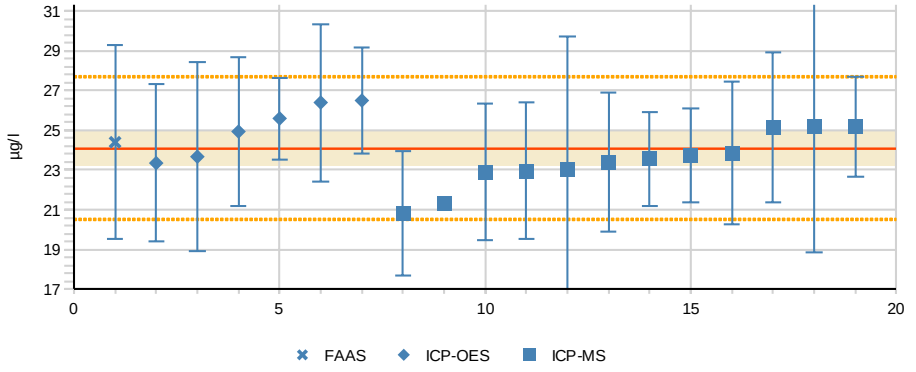
Measurand Zn Sample A1M



Measurand Zn Sample D2M

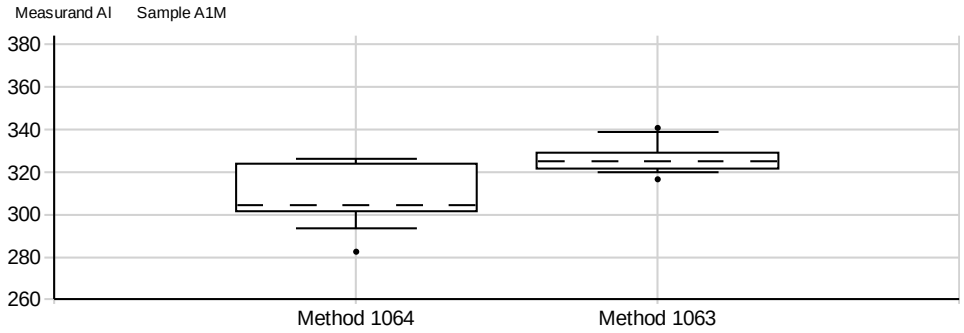


Measurand Zn Sample N3M



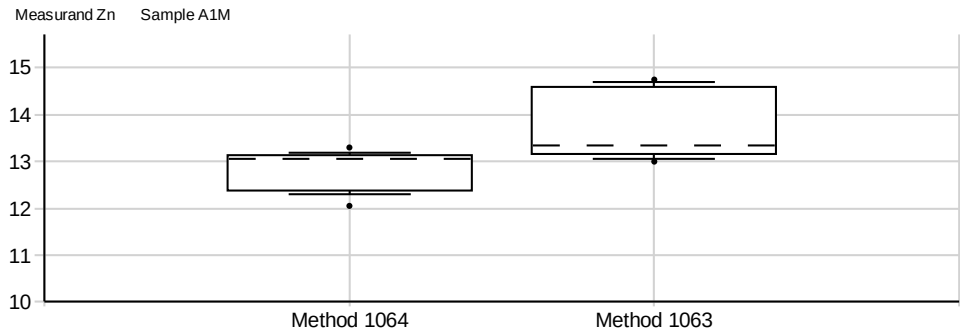
APPENDIX 11: Significant differences in the results reported using different methods

Boxplot figures: In the box the upper and lower limit included 50 % of the results. The dashed vertical line in the box is the median of the results. The vertical lines above and under the box describe the limits of 80 % of the results. The black dots describe the highest and smallest results within the center 90 % of the results.



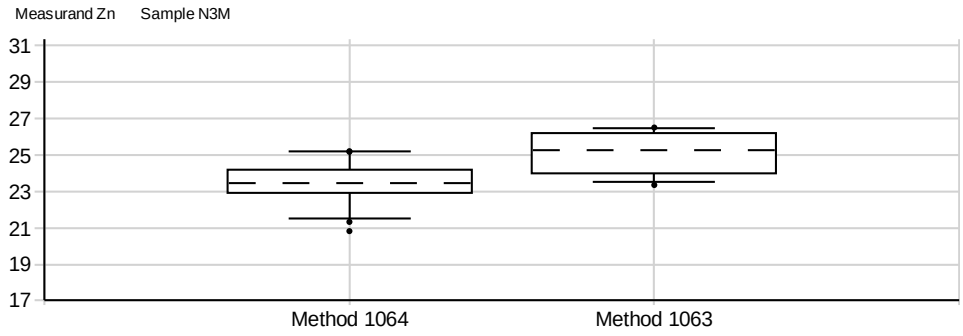
Method	n	Mean (µg/l)	Median (µg/l)	SD (µg/l)
ICP-MS: Method 1064	7	309	304	16
ICP-OES: Method 1063	8	327	325	8.3

n= number of results; SD= standard deviation



Method	n	Mean (µg/l)	Median (µg/l)	SD (µg/l)
ICP-MS: Method 1064	11	12.8	13.1	0.44
ICP-OES: Method 1063	5	13.8	13.4	0.83

n= number of results; SD= standard deviation

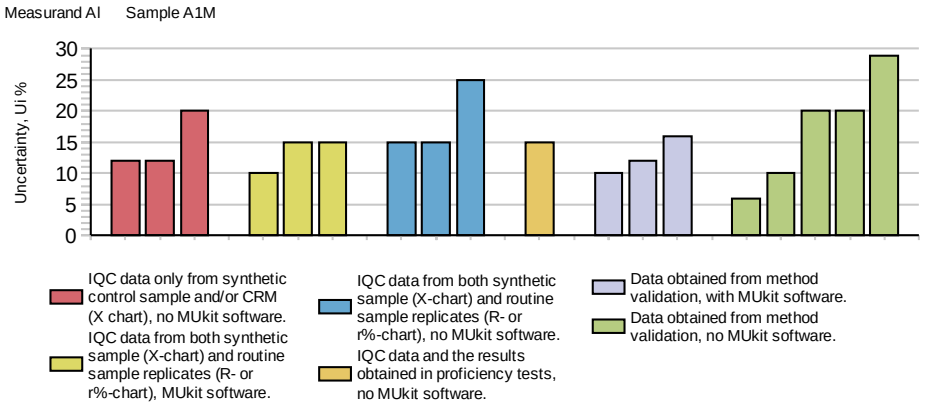


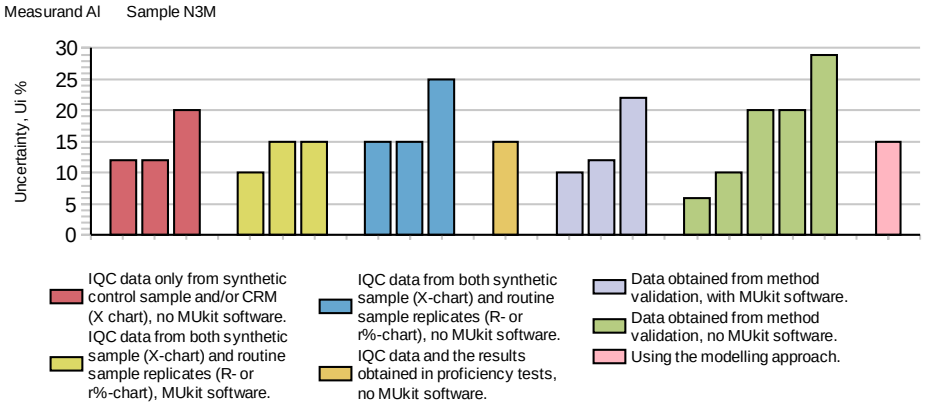
Method	n	Mean (µg/l)	Median (µg/l)	SD (µg/l)
ICP-MS: Method 1064	12	23.4	23.5	1.39
ICP-OES: Method 1063	6	25.1	25.3	1.34

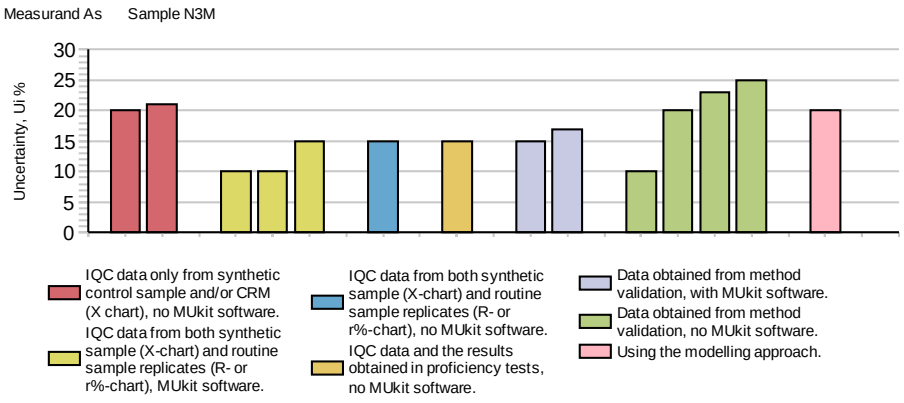
n= number of results; SD= standard deviation

APPENDIX 12: Estimation of the measurement uncertainties reported by the participants

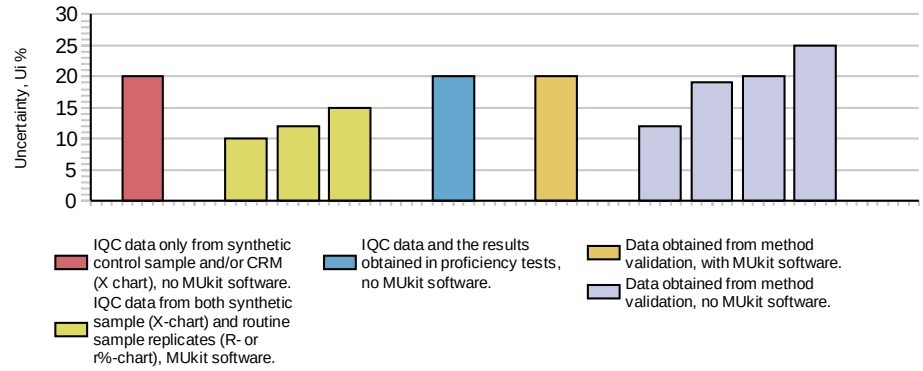
In example figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [6, 7] or using a modelling approach based [11, 12].



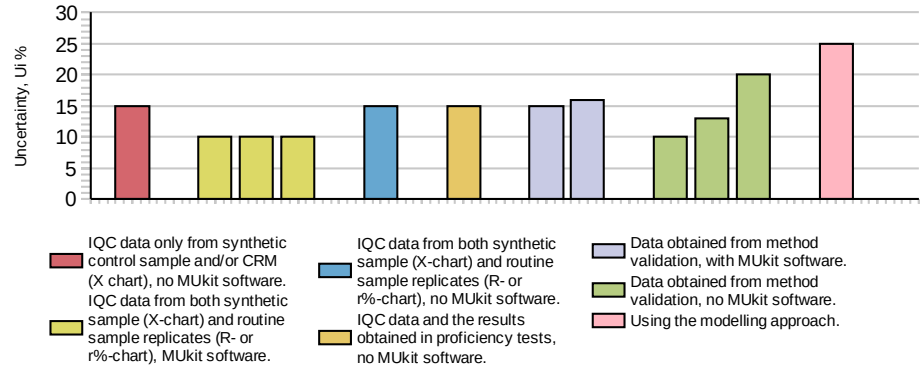




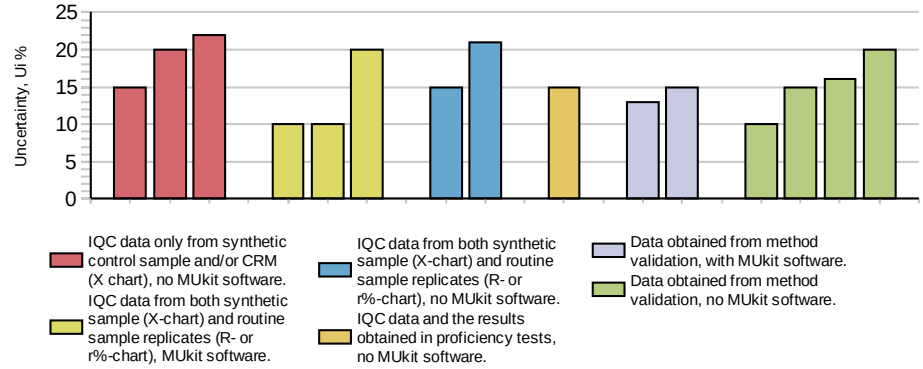
Measurand B Sample A1M



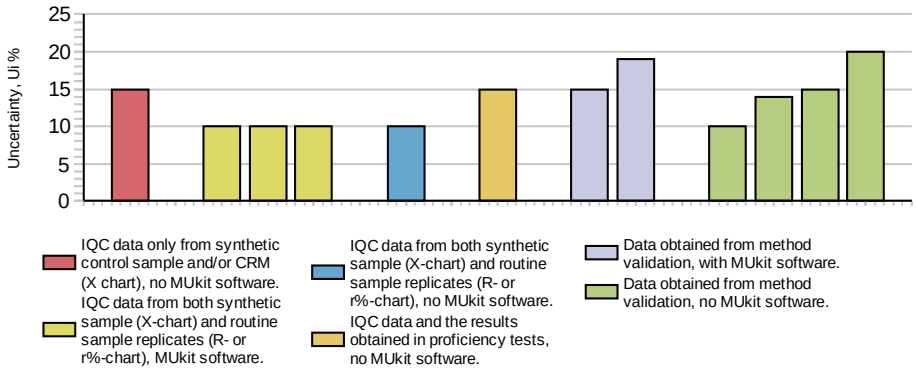
Measurand Ba Sample N3M



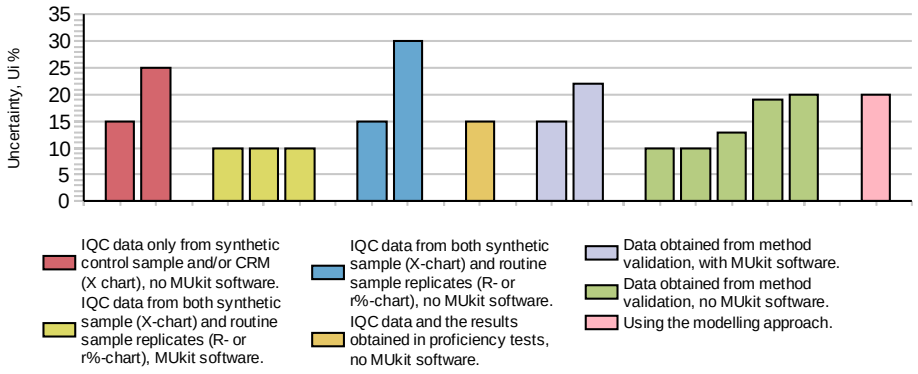
Measurand Cd Sample D2M



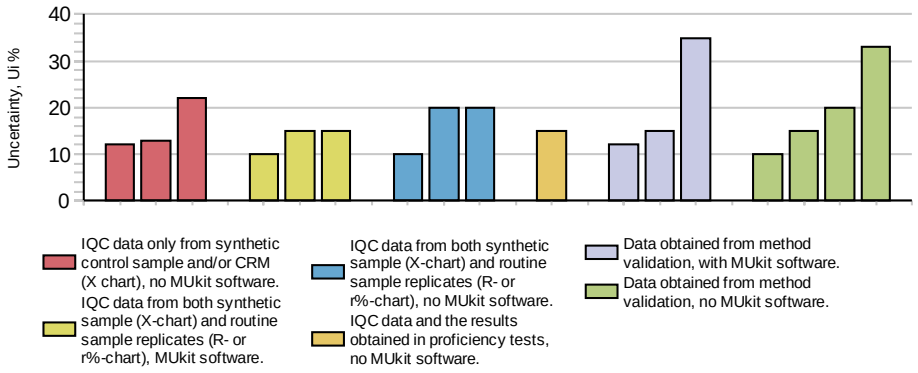
Measurand Co Sample D2M



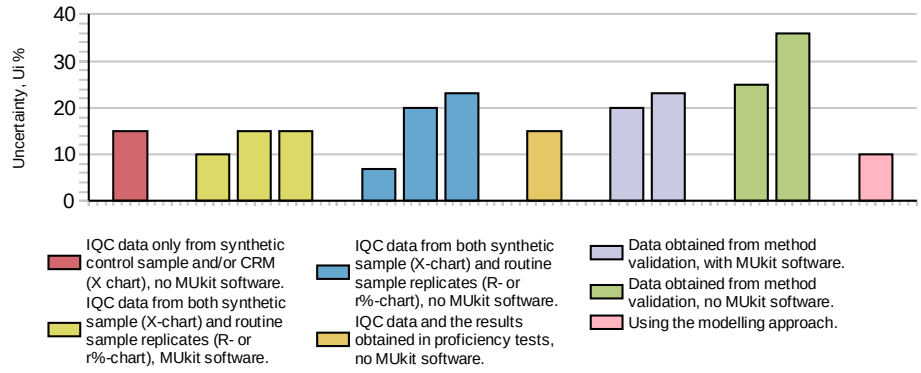
Measurand Cr Sample N3M



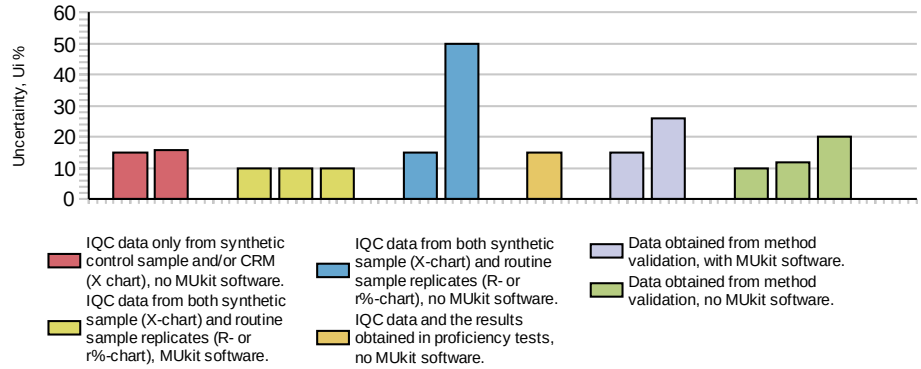
Measurand Fe Sample D2M



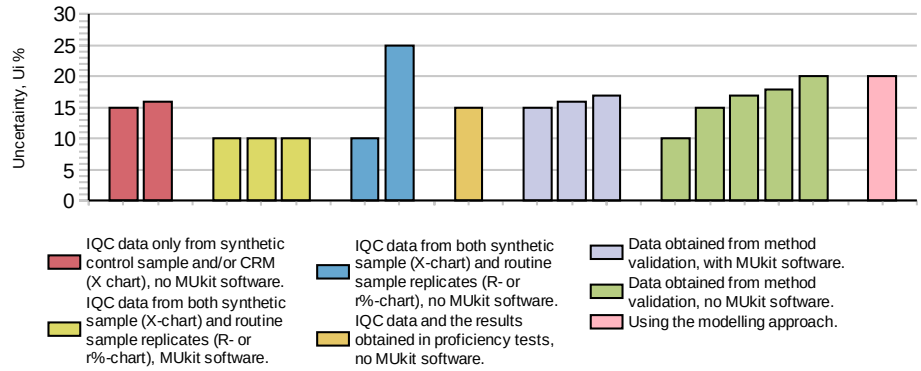
Measurand Hg Sample N3Hg

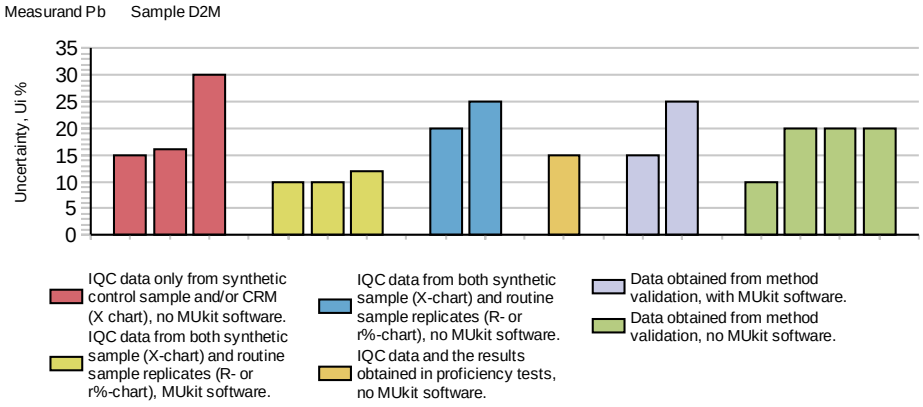


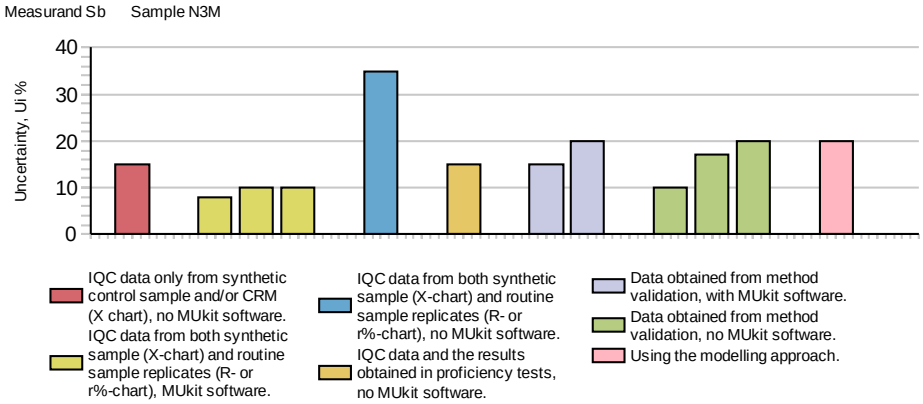
Measurand Mo Sample D2M

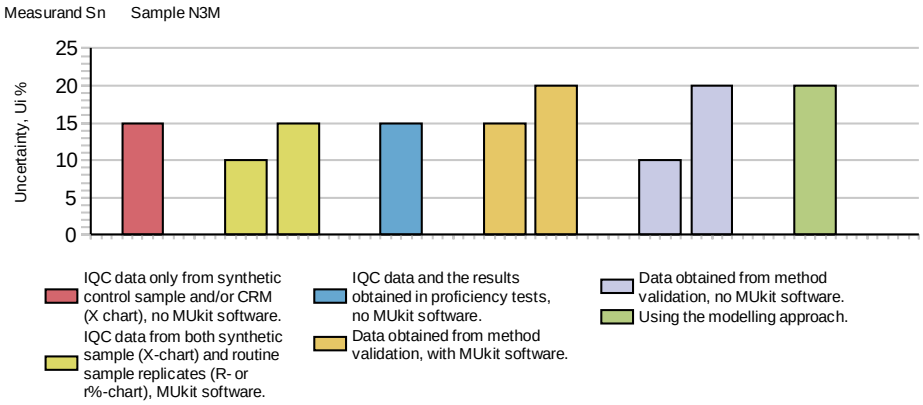


Measurand Ni Sample N3M

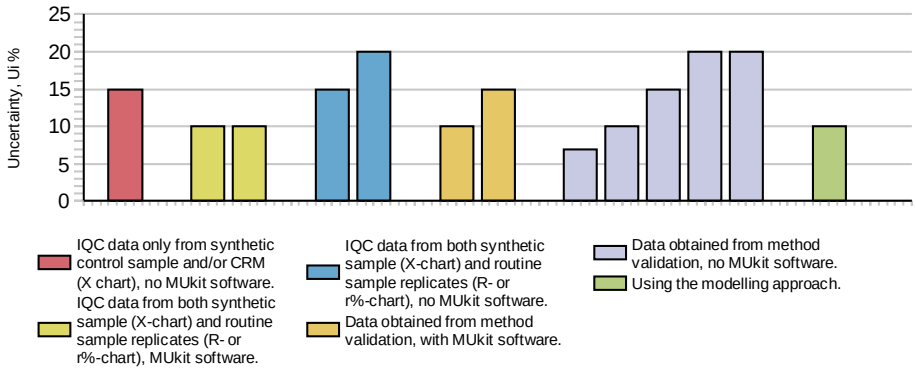



Measurand Pb Sample D2M
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, with MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.

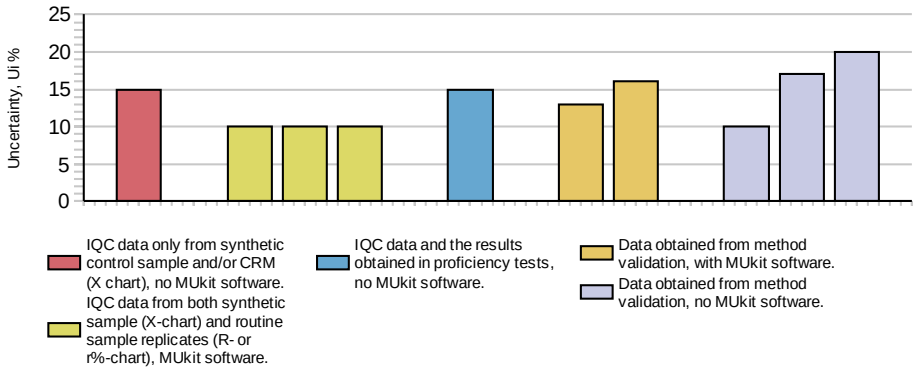

Measurand Sb Sample N3M
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, with MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand Sn Sample N3M
Uncertainty, Ui %
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, with MUkit software.

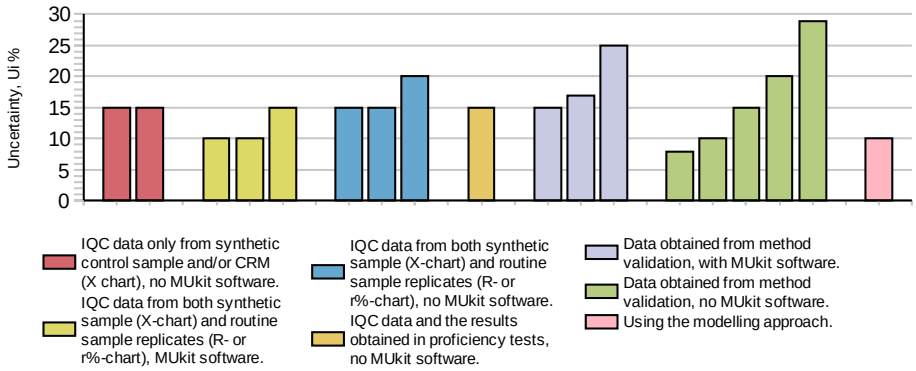
Measurand Stot Sample N3M



Measurand U Sample D2M



Measurand Zn Sample N3M



PROFICIENCY TEST SYKE 04/2017

FINNISH ENVIRONMENT INSTITUTE

ISBN 978-952-11-4865-1 (pbk.)
ISBN 978-952-11-4866-8 (PDF)
ISSN 1796-1718 (print)
ISSN 1796-1726 (Online)